Boron Compounds

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Isolation of a Three-Coordinate Boron Cation with a Boron–Sulfur Double Bond**

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Dedicated to Professor Hans-Ulrich Reißig on the occasion of his 65th birthday

Abstract: *The reaction of the bulky bis(imidazolin-2-iminato) ligand precursor (1,2-($L^{Mes}NH$)$_2$-C_2H_4)[OTs]$_2$ (**1**$^{2+}$2[OTs]$^-$; L^{Mes} = 1,3-dimesityl imidazolin-2-ylidene, OTs = p-toluenesulfonate) with lithium borohydride yields the boronium dihydride cation (1,2-($L^{Mes}N$)$_2$-C_2H_4)BH_2[OTs] (**2**$^+$[OTs]$^-$). The boronium cation **2**$^+$[OTs]$^-$ reacts with elemental sulfur to give the thioxoborane salt (1,2-($L^{Mes}N$)$_2$-C_2H_4)BS[OTs] (**3**$^+$[OTs]$^-$). The hitherto unknown compounds **1**$^{2+}$2[OTs]$^-$, **2**$^+$[OTs]$^-$, and **3**$^+$[OTs]$^-$ were fully characterized by spectroscopic methods and single-crystal X-ray diffraction. Moreover, DFT calculations were carried out to elucidate the bonding situation in **2**$^+$ and **3**$^+$. The theoretical, as well as crystallographic studies reveal that **3**$^+$ is the first example for a stable cationic complex of three-coordinate boron that bears a B=S double bond.*

In the course of the past decades considerable effort has been made to explore the nature of well-defined cationic molecular complexes of boron.[1] A common categorization of these compounds follows the coordination number of the boron center. Hence, the terms boronium-, borenium-, and borinium-cation refer to a four-, three-, and two-coordinate boron atom, respectively. It is important to take the location of the cationic charge into consideration, that is, its distribution across the boron site and the attached ligand system. Consequently, a boron-containing cation may not be a boron-centered cation at all and, thus, a different terminology would apply. Though a variety of three-coordinated boron cations have been described,[2] the chemistry of this subclass is still in the early stage of its development. Accordingly, taken aside examples with catecholate as the supporting ligand system, such as **I**[2a,3,4] (Figure 1) structurally characterized borenium ions with chalcogen atoms (E) bound to the boron center are surprisingly rare. Standing out in this context is the report of Curran and co-workers on the isolation of the dihydroxyborenium salt **II** (Figure 1) with very short B–O distances which suggests high double bond character between these atoms.[5] In comparison, the related borenium compound **III** (Figure 1) shows elongated B–O bond lengths.[6] Great attention is paid to the uncharged congeners and, as a result, there are several reports about main-group-element compounds marked by high degree of B=O double-bond and B≡O triple-bond character.[7,8]

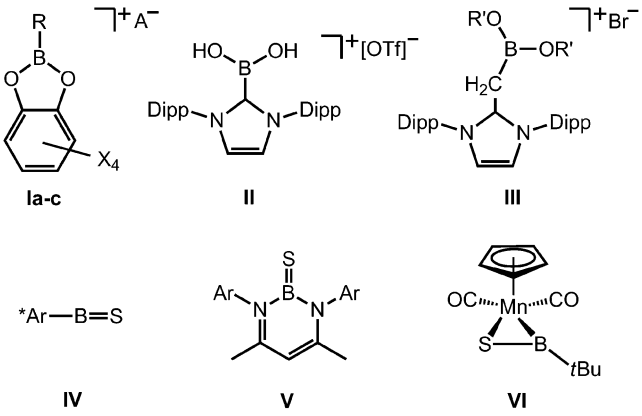

Figure 1. Selected structurally characterized borenium salts with chalcogen ligands (**I**–**III**; **Ia**: R = NEt_3, X = Cl, $A^- = [AlCl_4]^-$; **Ib**: R = P*t*Bu_3, X = H, $A^- = [HB(C_6F_5)_3]^-$; **Ic**: R = $OPEt_3$, X = H, $A^- = [$*closo*-1-H-$CB_{11}H_5Br_6]^-$; R′ = C_4H_8Br, Dipp = 2,6-di*iso*propylphenyl). The elusive thioxoborane **IV**, the β-diketiminato-stabilized thioxoborane **V** and the intermediate manganese complex **VI** (Ar* = 2,4,6-$(CH(SiMe_3)_2)_3$-C_6H_2; Ar = 2,6-Me_2-C_6H_3).

If the focus is shifted to molecular complexes of the heavier chalcogens, examples for B–E interactions of higher bond order are almost unknown. The existence of the transient thioxoborane **IV** has been proposed in seminal work by Tokitoh et al. (Figure 1).[9] Since then 20 years have passed and only two electron-precise complexes featuring boron–chalcogen double bonds of the higher homologues have been isolated, that is, the thioxoborane **V** and its selenium analogue (Figure 1).[10] The manganese complex **VI** was also proposed as a transient intermediate, but structural characterization of this compound is hampered by its elusive nature (Figure 1).[11] Hitherto, a cationic molecular complex of boron with an inherent B=E double bond has not been fully characterized. Herein, we describe the first isolation of a cationic boron compound with a B=S double bond.

Recently, we reported on the application of several imidazolin-2-iminato complexes of boron-[12] and aluminum dihydride[13] in C–N and S–S bond activations, respectively.

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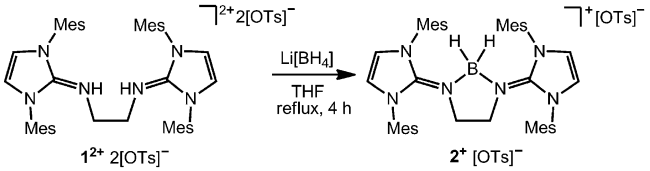
We ascribed the observed reactivity as being largely due to the strongly electron-donating character of this ligand. Interestingly, a Review on the main-group-element chemistry,[14] as well as the rich transition-metal chemistry[15] of this ligand system was also published.[16] Taking into account this background we set out to exploit the properties of the imidazolin-2-imino group for new methods of bond activation.

The observation that yellow sulfur readily reacts with imino-substituted aluminum hydrides[13b,17] prompted us to investigate related conversions with the lower homologue boron. Notably, while the reactivity of N-heterocyclic carbene (NHC)-stabilized borohydrides with diaryl disulfides has recently emerged,[18] reactions between molecular borohydrides and elemental sulfur are negligible.[10,19,20] We conceived that a bulky congener of the bisiminato ligand 1,2-$(Me_2L^{iPr}N)_2$-C_2H_4[15a] (Me_2L^{iPr} = 1,3-di*iso*propyl-4,5-dimethyl imidazolin-2-ylidene) might lead to a suitable borohydride because 1) unlike complexes of monoimino-substituted borohydride with NHC it would not be prone to the hydride-mediated ring-expansion reaction,[12] 2) the ethylene linker could yield a chelate-fashioned complex with concomitant gain in thermodynamic stability, and 3) each imino group may act as a strong 2σ- and 2π electron donor, thus, compared to NHC-stabilized iminoborohydride, the reactivity of the BH moiety towards electrophiles would be enhanced.

The reaction of the bis(iminiumhydrotosylate) $\mathbf{1}^{2+}$2-$[OTs]^-$ with one equivalent of lithium borohydride in THF gives access to the boron dihydride $\mathbf{2}^+[OTs]^-$ in good yield (58%, Scheme 1). Though poorly soluble in the reaction



Scheme 1. Conversion of the bis(imidazolin-2-iminium) salt $\mathbf{1}^{2+}$2$[OTs]^-$ into the borohydride $\mathbf{2}^+[OTs]^-$.

medium the product readily dissolves in chloroform, dichloromethane, or acetonitrile. Notably, related boronium cations bearing carbon-,[21] nitrogen-,[22] or phosphorus-based[23] ligands at the boron center have been described in the literature. In the $^{11}B\{^1H\}$ NMR spectrum of $\mathbf{2}^+[OTs]^-$ (CD_3CN) a signal at $\delta = -8.6$ ppm ($h_{1/2} = 240$ Hz) indicates the presence of a four-coordinate boron center and the resonance broadens to $h_{1/2} = 360$ Hz in the proton-coupled ^{11}B NMR analysis, though J coupling is not resolved. It is noteworthy, that in the ^1H NMR spectrum (CD_3CN) a very broad signal centered around $\delta = 1.38$ ppm integrating to two protons, turns into a sharp singlet in the $^1H\{^{11}B\}$ NMR analysis and, thus, is assigned to the hydrogen atoms bond to the boron center of $\mathbf{2}^+[OTs]^-$.

Crystals for the X-ray diffraction study of $\mathbf{2}^+[OTs]^-$-$(CH_3CN)_2$ were obtained by slow evaporation of solvent from its acetonitrile solution (Figure 2). The positions of the

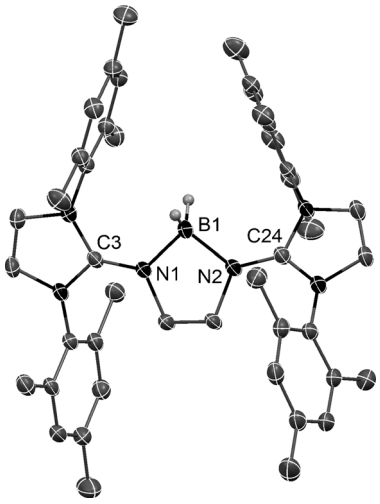
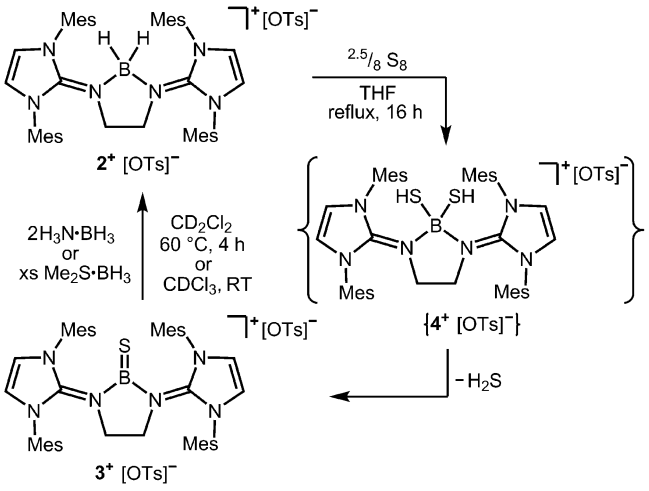


Figure 2. Molecular structure of $\mathbf{2}^+$. Hydrogen atoms except on boron have been omitted for clarity. Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and bond angle [°]: B1–N1 1.577(5), B1–N2 1.573(5), C3–N1 1.317(5), C24–N2 1.318(4); N1-B1-N2 98.6(3).

hydride atoms were found in the electron-density map and the N-B-N bond angle of 98.6(3)° confirms tetrahedral coordination of the boron center . The B–N distances in $\mathbf{2}^+$ amount to 1.573(5) Å and 1.577(5) Å. This is longer than the B–N bond of 1.524(2) Å in $L^{Mes}N(BH_2)L^{Mes}$ which bears a trivalent nitrogen atom bound to the boron center.[12]

The reaction of $\mathbf{2}^+[OTs]^-$ with $^{2.5}/_8$ equivalents of yellow sulfur requires about 16 h in boiling THF to give, in high yield (isolated: 78%), the thioxoborane $\mathbf{3}^+[OTs]^-$ (Scheme 2). In the ^1H NMR spectrum (CD_3CN) of $\mathbf{3}^+[OTs]^-$ the characteristic singlet arising from the four hydrogen atoms of the imidazoline-ligand backbones is observed at significantly lower field ($\delta(^1H) = 7.22$ ppm) than the respective resonance of the parent borohydride $\mathbf{2}^+$ ($\delta(^1H) = 6.55$ ppm, CD_3CN). Similarly, though less pronounced, the signal produced by the carbon atoms of the imidazoline ligand backbone is shifted



Scheme 2. Conversion of the borohydride $\mathbf{2}^+[OTs]^-$ into the thioxoborane salt $\mathbf{3}^+[OTs]^-$ by the proposed intermediate $\{\mathbf{4}^+[OTs]^-\}$.

downfield from $\delta = 118.7$ ppm for $\mathbf{2}^+$ to $\delta = 121.3$ ppm for $\mathbf{3}^+$ in the $^{13}C\{^1H\}$ NMR analysis (CD_3CN). These changes in the NMR spectroscopic characteristics of the bisiminato ligand coincide with the formation of a thioxoborane moiety in $\mathbf{3}^+$ with a trigonal-planar coordinate boron center as revealed by our X-ray diffraction study. Moreover, the ^{11}B NMR analysis (CD_3CN) reveals a broad signal at $\delta = 33.9$ ppm ($h_{1/2} = 510$ Hz) which is in agreement with the chemical shift reported for the boron nucleus in **V** ($\delta(^{11}B) = 36.79$ ppm, C_6D_6).[10] The stoichiometric composition of $\mathbf{3}^+$ is confirmed by ESI high-resolution mass spectrometry.

From Et_2O/CH_3CN solution $\mathbf{3}^+[OTs]^-$ crystallized in the monoclinic space group *C*2/*c* (Figure 3). The sum of the bond angles around the boron atom in $\mathbf{3}^+$ is in good approximation 360°. As a consequence of the trigonalization at the boron center the B–N bond lengths significantly decrease to 1.483(5) Å and 1.493(5) Å. Remarkably, the distance between the boron and the sulfur atom is only 1.710(5) Å which is shorter than the B=S bond length in the related thioxoborane **V** (1.741(2) Å) that had been reported as the first electron-precise compound featuring a B=S double bond.[10] To our knowledge, this B=S bond in $\mathbf{3}^+$ is the shortest bond between boron and sulfur reported for a molecular complex. We assume that the cationic character of this thioxoborane strengthens the interaction between the boron and the sulfur atom. For comparison, the B–S distance in the trigonal borane $Mes_2B(SCH_3)$ is 1.787(6) Å.[24] Interestingly, the C=N bond lengths of the two imino groups in $\mathbf{3}^+$ are 1.359(4) Å and 1.363(4) Å which is longer than observed for the boronium cation $\mathbf{2}^+$ (1.317(5) Å and 1.318(4) Å). Note that the solid-state structure of $\mathbf{3}^+[OTs]^-$ reveals no bonding interaction between the boron site and the tosylate anion.

For greater insight into the bonding situation, we subjected the cationic parts ($\mathbf{2}^+$ and $\mathbf{3}^+$) to DFT calculations at the B3LYP/6-311G(d) level of theory. The NBO charge at the boron center in $\mathbf{2}^+$ amounts to +0.263 and significantly increases to +0.634 upon transformation to the thioxoborane cation $\mathbf{3}^+$. As expected, the B–S vector in $\mathbf{3}^+$ is polarized towards the sulfur atom (NBO charge at S = −0.578). It is of note that the Wiberg Bond Index (WBI) for the B–S bond in $\mathbf{3}^+$ is 1.739 which indicates a high double-bond character, particularly in light of the unequal charge distribution between the boron and the sulfur atom. The WBI of the C=N bonds of the two imino groups in $\mathbf{3}^+$ are both determined to 1.134 whereas the respective values in $\mathbf{2}^+$ are 1.317 and 1.294. These values show that the imino bonds are significantly weakened upon transformation of $\mathbf{2}^+$ to $\mathbf{3}^+$ presumably by the shift of electron density from the ligand system into the trigonal-planar boron site. Investigation of the frontier Kohn–Sham orbitals (Figure 4) of $\mathbf{3}^+$ reveals that the HOMO essentially corresponds to a lone pair located at the sulfur atom, whereas the HOMO−1 essentially comprises a B=S π-bonding orbital. The LUMO of $\mathbf{3}^+$ is mainly delocalized across the imidazoline rings of the ligand, though, a considerable contribution is made by π* components located at the BN_2 moiety. The HOMO and HOMO−1 of the related thioxoborane **V** have Kohn–Sham orbitals of very similar composition to $\mathbf{3}^+$.[10] However, in contrast to $\mathbf{3}^+$ the LUMO in **V** shows no contribution from the boron center. This difference may be attributed to the ionic nature of $\mathbf{3}^+[OTs]^-$.

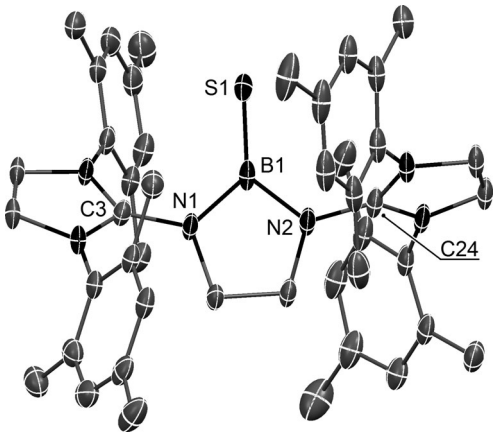


Figure 3. Molecular structure of $\mathbf{3}^+$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: B1–N1 1.493(5), B1–N2 1.483(5), B1–S1 1.710(5), C3–N1 1.359(4), C24–N2 1.363(4); N1-B1-N2 100.6(3), N1-B1-S1 129.7(3), N2-B1-S1 129.8(3).

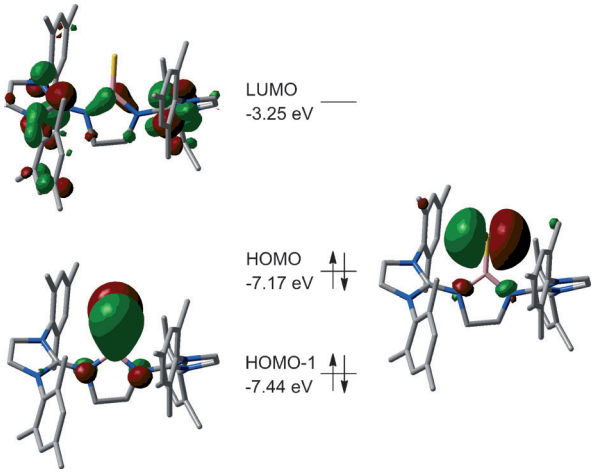


Figure 4. Selected molecular orbitals for the thioxoborane cation $\mathbf{3}^+$ calculated at the B3LYP/6-311G(d) level of theory. Boron (pink), sulfur (yellow), nitrogen (blue), and carbon (gray).

With respect to the reaction mechanism for the formation of $\mathbf{3}^+[OTs]^-$ it is of note that the reaction of $\mathbf{2}^+[OTs]^-$ with only $^1/_8$ equivalent of S_8 resulted in the isolation of a distinct mixture of solids consisting of $\mathbf{2}^+[OTs]^-$ and $\mathbf{3}^+[OTs]^-$ in a 1:2 ratio. Thus, we propose that this transformation proceeds by the elimination of hydrogen sulfide from the double insertion product $\{\mathbf{4}^+[OTs]^-\}$ rather than by the release of dihydrogen from a conceivable boron hydride hydrogensulfide species (Scheme 2).[25] Even though we cannot present evidence for an intermediate hydrogensulfide species, its existence is supported by related reactions of borohydrides with elemental sulfur described in the literature.[9,10,19]

We were curious if the polar character of the B=S double bond could be exploited to synthesize a boron-centered hydrogensulfide, thus, presenting indirect evidence for the presumed insertion of sulfur into the BH bond of $\mathbf{2}^+$ (Scheme 2). We chose $H_3N{\cdot}BH_3$ as a hydrogen-transfer reagent because with its combination of protic and hydridic reactive sites it resembles an activated form of dihydrogen.[26] The treatment of $\mathbf{3}^+[OTs]^-$ with two equivalents of ammonia-borane in CD_2Cl_2 at elevated temperature resulted in near-quantitative transformation to $\mathbf{2}^+[OTs]^-$, based on NMR spectroscopy. Interestingly, the reaction of the thioxoborane with an excess of borane dimethylsulfide in $CDCl_3$ at room temperature yielded the borohydride in a similar manner. We assume that the reactive pathway from the thioxoborane compound to the parent borohydride proceeds by coordination of the sulfur atom in $\mathbf{3}^+$ to the hydroborane (note: the HOMO of $\mathbf{3}^+$ is mainly located at the sulfur center).

In conclusion we have described the synthesis and isolation of $\mathbf{3}^+[OTs]^-$, which is the first cationic electron-precise complex of boron that bears a B=S double bond. This compound is closely related to the elusive thioxoborane species. Access to $\mathbf{3}^+[OTs]^-$ is granted through the borohydride $\mathbf{2}^+[OTs]^-$, which features a bis(imidazolin-2-iminato) ligand. We account the stability of the trigonal-planar site in $\mathbf{3}^+$ to the pronounced π electron-donating character of the imidazolin-2-imino group. Preliminary investigation of the reactivity of $\mathbf{3}^+[OTs]^-$ revealed that hydroboranes, such as $H_3N{\cdot}BH_3$ convert the thioxoborane back into its borohydride precursor. Further studies on $\mathbf{3}^+$ will focus on its use as a thionation reagent, the electrophilicity of the boron center, and the Lewis base character of the sulfur atom.

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[1] a) W. E. Piers, S. C. Bourke, K. D. Conroy, *Angew. Chem. Int. Ed.* **2005**, *44*, 5016 – 5036; *Angew. Chem.* **2005**, *117*, 5142 – 5163; b) T. S. De Vries, A. Prokofjevs, E. Vedejs, *Chem. Rev.* **2012**, *112*, 4246 – 4282; c) H. Zhao, L. A. Leamer, F. P. Gabbaï, *Dalton Trans.* **2013**, *42*, 8164 – 8178; d) I. B. Sivaev, V. I. Bregadze, *Coord. Chem. Rev.* **2014**, *270 – 271*, 75 – 88; e) C. Reus, M. Wagner, *Nat. Chem.* **2014**, *6*, 466 – 467.

[2] For selected recent examples of borenium cations see: a) A. Del Grosso, P. J. Singleton, C. A. Muryn, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2011**, *50*, 2102 – 2106; *Angew. Chem.* **2011**, *123*, 2150 – 2154; b) B. Inés, M. Patil, J. Carreras, R. Goddard, W. Thiel, M. Alcarazo, *Angew. Chem. Int. Ed.* **2011**, *50*, 8400 – 8403; *Angew. Chem.* **2011**, *123*, 8550 – 8553; c) C. I. Someya, S. Inoue, C. Präsang, E. Irran, M. Driess, *Chem. Commun.* **2011**, *47*, 6599 – 6601; d) H. B. Mansaray, A. D. L. Rowe, N. Phillips, J. Niemeyer, M. Kelly, D. A. Addy, J. I. Bates, S. Aldridge, *Chem. Commun.* **2011**, *47*, 12295 – 12297; e) J. M. Farrell, J. A. Hatnean, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 15728 – 15731; f) V. Bagutski, A. Del Grosso, J. A. Carrillo, I. A. Cade, M. D. Helm, J. R. Lawson, P. J. Singleton, S. A. Solomon, T. Marcelli, M. J. Ingleson, *J. Am. Chem. Soc.* **2013**, *135*, 474 – 487; g) E. R. Clark, A. Del Grosso, M. J. Ingleson, *Chem. Eur. J.* **2013**, *19*, 2462 – 2466; h) J. Chen, R. A. Lalancette, F. Jäkle, *Chem. Commun.* **2013**, *49*, 4893 – 4895; i) J. R. Lawson, E. R. Clark, I. A. Cade, S. A. Solomon, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2013**, *52*, 7518 – 7522; *Angew. Chem.* **2013**, *125*, 7666 – 7670; j) S. E. Denmark, Y. Ueki, *Organometallics* **2013**, *32*, 6631 – 6634; k) T. Stahl, K. Müther, Y. Ohki, K. Tatsumi, M. Oestreich, *J. Am. Chem. Soc.* **2013**, *135*, 10978 – 10981.

[3] M. A. Dureen, A. Lough, T. M. Gilbert, D. W. Stephan, *Chem. Commun.* **2008**, 4303 – 4305.

[4] A. Del Grosso, R. G. Pritchard, C. A. Muryn, M. J. Ingleson, *Organometallics* **2010**, *29*, 241 – 249.

[5] A. Solovyev, S. J. Geib, E. Lacôte, D. P. Curran, *Organometallics* **2012**, *31*, 54 – 56.

[6] Y. Wang, M. Y. Abraham, R. J. Gilliard, Jr., D. R. Sexton, P. Wei, G. H. Robinson, *Organometallics* **2013**, *32*, 6639 – 6642.

[7] a) D. Vidovic, J. A. Moore, J. N. Jones, A. H. Cowley, *J. Am. Chem. Soc.* **2005**, *127*, 4566 – 4567; b) Y. Wang, H. Hu, J. Zhang, C. Cui, *Angew. Chem. Int. Ed.* **2011**, *50*, 2816 – 2819; *Angew. Chem.* **2011**, *123*, 2868 – 2871; c) Y. K. Loh, C. C. Chong, R. Ganguly, Y. Li, D. Vidovic, R. Kinjo, *Chem. Commun.* **2014**, *50*, 8561 – 8564.

[8] a) H. Braunschweig, K. Radacki, A. Schneider, *Science* **2010**, *328*, 345 – 347; b) H. Braunschweig, K. Radacki, A. Schneider, *Chem. Commun.* **2010**, *46*, 6473 – 6475.

[9] N. Tokitoh, M. Ito, R. Okazaki, *Tetrahedron Lett.* **1996**, *37*, 5145 – 5148.

[10] H. Wang, J. Zhang, H. Hu, C. Cui, *J. Am. Chem. Soc.* **2010**, *132*, 10998 – 10999.

[11] J. Bauer, H. Braunschweig, A. Damme, J. O. C. Jiminez-Halla, T. Kramer, K. Radacki, R. Shang, E. Siedler, Q. Ye, *J. Am. Chem. Soc.* **2013**, *135*, 8726 – 8734.

[12] D. Franz, S. Inoue, *Chem. Asian J.* **2014**, *9*, 2083 – 2087.

[13] a) D. Franz, E. Irran, S. Inoue, *Dalton Trans.* **2014**, *43*, 4451 – 4461; b) D. Franz, S. Inoue, *Chem. Eur. J.* **2014**, *20*, 10645 – 10649.

[14] a) N. Kuhn, R. Fawzi, M. Steimann, J. Wiethoff, *Z. Anorg. Allg. Chem.* **1997**, *623*, 554 – 560; b) N. Kuhn, U. Abram, C. Maichle-Mößmer, J. Wiethoff, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1121 – 1124; c) N. Kuhn, M. Grathwohl, M. Steimann, G. Henkel, *Z. Naturforsch. B* **1998**, *53*, 997 – 1003; d) N. Kuhn, M. Göhner, M. Grathwohl, J. Wiethoff, G. Frenking, Y. Chen, *Z. Anorg. Allg. Chem.* **2003**, *629*, 793 – 802; e) R. Kinjo, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 5930 – 5933; *Angew. Chem.* **2010**, *122*, 6066 – 6069; f) S. Inoue, K. Leszczyńska, *Angew. Chem. Int. Ed.* **2012**, *51*, 8589 – 8593; *Angew. Chem.* **2012**, *124*, 8717 – 8721; g) F. Dielmann, O. Back, M. Henry-Ellinger, P. Jerabek, G. Frenking, G. Bertrand, *Science* **2012**, *337*, 1526 – 1528.

[15] a) D. Petrovic, T. Glöge, T. Bannenberg, C. G. Hrib, S. Randoll, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2007**, 3472 – 3475; b) D. Petrovic, L. M. R. Hill, P. G. Jones, W. B. Tolman, M. Tamm, *Dalton Trans.* **2008**, 887 – 894; c) S. Beer, K. Brandhorst, C. G. Hrib, X. Wu, B. Haberlag, J. Grunenberg, P. G. Jones, M. Tamm, *Organometallics* **2009**, *28*, 1534 – 1545; d) T. Glöge, D. Petrovic, C. G. Hrib, C. Daniliuc, E. Herdtweck, P. G. Jones, M. Tamm, *Z. Anorg. Allg. Chem.* **2010**, *636*, 2303 – 2308; e) A. G. Trambitas, J. Yang, D. Melcher, C. G. Daniliuc, P. G. Jones, Z. Xie, M. Tamm, *Organometallics* **2011**, *30*, 1122 – 1129; f) D. Shoken, M. Sharma, M. Botoshansky, M. Tamm, M. S. Eisen, *J. Am. Chem. Soc.* **2013**, *135*, 12592 – 12595; g) K. Nomura, B. K. Bahuleyan, S. Zhang, P. M. V. Sharma, S. Katao, A. Igarashi, A. Inagaki, M. Tamm, *Inorg. Chem.* **2014**, *53*, 607 – 623; h) I. S. R. Karmel, M. Botoshansky, M. Tamm, M. S. Eisen, *Inorg. Chem.* **2014**, *53*, 694 – 696.

[16] X. Wu, M. Tamm, *Coord. Chem. Rev.* **2014**, *260*, 116 – 138.

[17] a) V. Jancik, Y. Peng, H. W. Roesky, J. Li, D. Neculai, A. M. Neculai, R. Herbst-Irmer, *J. Am. Chem. Soc.* **2003**, *125*, 1452 – 1453; b) S. González-Gallardo, V. Jancik, R. Cea-Olivares, R. A. Toscano, M. Moya-Cabrera, *Angew. Chem. Int. Ed.* **2007**, *46*, 2895 – 2898; *Angew. Chem.* **2007**, *119*, 2953 – 2956.

[18] a) X. Pan, A.-L. Vallet, S. Schweizer, K. Dahbi, B. Delpech, N. Blanchard, B. Graff, S. J. Geib, D. P. Curran, J. Lalevée, E. Lacôte, *J. Am. Chem. Soc.* **2013**, *135*, 10484 – 10491; b) S. Telitel, A.-L. Vallet, S. Schweizer, B. Delpech, N. Blanchard, F. Morlet-Savary, B. Graff, D. P. Curran, M. Robert, E. Lacôte, J. Lalevée, *J. Am. Chem. Soc.* **2013**, *135*, 16938 – 16947.

[19] a) N. Tokitoh, M. Ito, R. Okazaki, *Organometallics* **1995**, *14*, 4460 – 4462; b) M. Ito, N. Tokitoh, R. Okazaki, *Organometallics* **1997**, *16*, 4314 – 4319.

[20] For selected examples from the field of borane-cluster chemistry see: a) J. Holub, J. D. Kennedy, T. Jelínek, B. Štíbr, *J. Chem. Soc., Dalton Trans.* **1994**, 1317 – 1323; b) T. Jelínek, J. D. Kennedy, B. Štíbr, M. Thornton-Pett, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1599 – 1601; *Angew. Chem.* **1994**, *106*, 1663 – 1665; c) H. Binder, M. Hein, *Coord. Chem. Rev.* **1997**, *158*, 171 – 232; d) Z. Janoušek, J. Holub, D. Hnyk, M. G. S. Londesborough, R. K. Shoemaker, *Polyhedron* **2003**, *22*, 3541 – 3545.

[21] D. A. Ruiz, M. Melaimi, G. Bertrand, *Chem. Commun.* **2014**, *50*, 7837 – 7839.

[22] K. Wang, Y. Zhang, D. Chand, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* **2012**, *18*, 16931 – 16937.

[23] a) M. Sigl, A. Schier, H. Schmidbaur, *Chem. Ber.* **1997**, *130*, 1411 – 1416; b) Y. Yamamoto, T. Koizumi, K. Katagiri, Y. Furuya, H. Danjo, T. Imamoto, K. Yamaguchi, *Org. Lett.* **2006**, *8*, 6103 – 6106; c) K. Owsianik, R. Chauvin, A. Balińska, M. Wieczorek, M. Cypryk, M. Mikołajczyk, *Organometallics* **2009**, *28*, 4929 – 4937.

[24] M. T. Ashby, N. A. Sheshtawy, *Organometallics* **1994**, *13*, 236 – 243.

[25] The relative amounts of $\mathbf{2}^+$ and $\mathbf{3}^+$ in the isolated solid mixture deviates from the ideal 1:1 ratio mainly because of the higher solubility of $\mathbf{2}^+[\mathrm{OTs}]^-$.

[26] A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, *110*, 4023 – 4078.

