

Boryllithium: A novel boron nucleophile and its application in the synthesis of borylmetal complexes*

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Abstract: The first boryl anion, boryllithium, was synthesized by a reduction of bromoborane precursor using lithium naphthalenide in tetrahydrofuran (THF) solvent at $-45\text{ }^{\circ}\text{C}$. Structural and spectroscopic study revealed an ionic character of B–Li bond. Boryllithium could be utilized as a source of boryl ligand in the transition-metal chemistry. Structural and spectroscopic features of the resulting boryl complexes confirmed the large trans influence of boryl ligand.

Keywords: boron; lithium; boryl complex; boryl anion; crystal structure.

INTRODUCTION

For most of the *p*-block elements in the second row of the periodic table, anions can be prepared as lithium salts, such as lithium fluoride (LiF), lithium hydroxide (LiOH), lithium amide (LiNH₂), and methyllithium (H₃CLi) [1]. However, there have been no direct observations of the lithium salt of anionic boron atom, boryllithium (a parent H₂B⁻Li or its analog) [2]. Since 1952, three examples [3–5] have been reported asserting the existence of alkali metal salts of anionic organoboron compounds as reactive intermediates, but none of these studies succeeded in spectroscopic characterization or isolation of the boryl anions [6–16]. This limitation for availability of boryl anion also narrows the chemistry of boryl transition-metal complexes [17–22], which show unique catalytic activity [23–29]. In fact, the following three types of reactions are the major methodologies to introduce a boryl ligand [17–22]: (1) salt elimination through the reaction of anionic metal carbonyl complexes with haloboranes [30]; (2) oxidative addition of a boron–heteroatom bond to low-valent transition metals [31]; and (3) σ -bond metathesis reactions between alkyl metal complexes and hydroboranes in the presence of light [32] or oxygen-substituted metal complexes and diborane [33–35]. Thus, a new and general methodology for the synthesis of boryl complexes by use of boryl anion would enable access to new types of boryl complexes. Here, we briefly review our recent discovery of boryllithium, which can be considered as a boryl anion, and its substitution onto the metal center of transition-metal halides [36–38].

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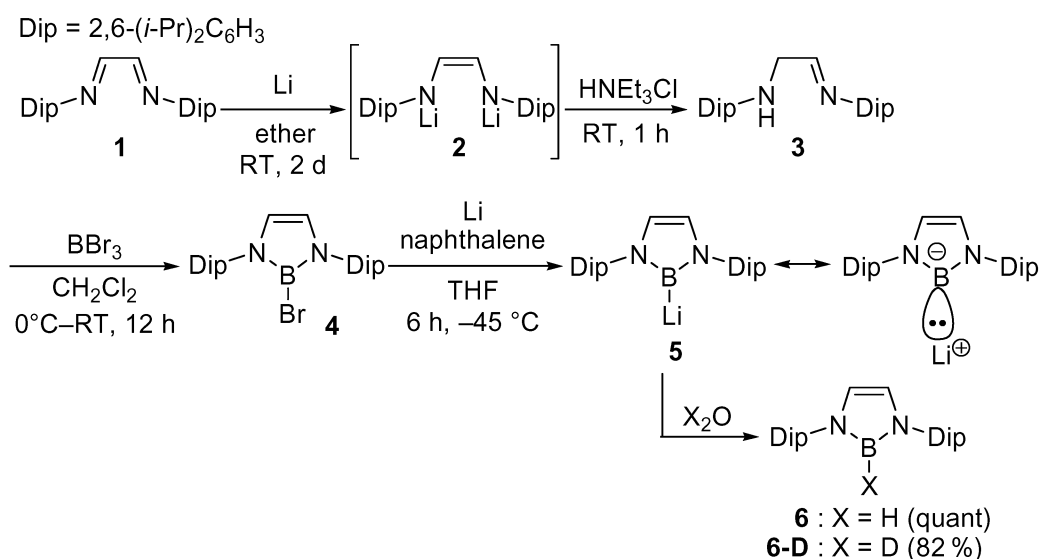
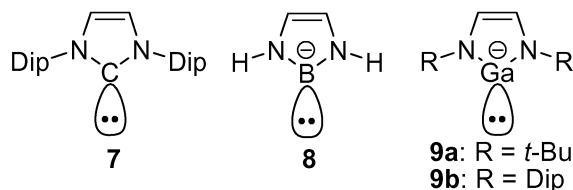
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RESULTS AND DISCUSSION

Synthesis, structure, and reactivity of boryllithium

Synthesis of boryllithium

Scheme 1 illustrates the synthesis of boryllithium **5**. The B–Li bond of boryllithium can be drawn as a resonance between a covalent and an ionic bond. The isoelectronic relation of the boryl anion to a singlet carbene prompted us to synthesize diaminoboryllithium **5** [39] as an isoelectronic analog of stable *N*-heterocyclic carbene **7** (Fig. 1) [40,41]. Also, the parent *N*-heterocyclic boryl anion **8** was predicted to realize aromatic stabilization by the five-membered ring structure containing two nitrogen atoms [42,43]. The nitrogen-containing five-membered ring structure has led to successful isolation of a free anionic gallium(I) species **9a,b**, which are heavier congeners of boryl anion [44,45]. Large 2,6-diisopropylphenyl groups were introduced on the nitrogen atoms to prevent the boryl radical intermediates from dimerizing to diborane [5,46–48]. A bromoborane precursor (**4**) [36,37] was synthesized in 77 % yield from diimine **1** [49]. The bromoborane **4** was successfully reduced to the boryllithium **5** with the use of a combination of lithium powder and naphthalene in tetrahydrofuran (THF) at $-45\text{ }^{\circ}\text{C}$. The reaction of **5** with water quantitatively gave a hydroborane **6** [50]. Treatment of **5** with D_2O afforded the corresponding deuterioborane **6-D** in 82 % yield, which indicates that **6** was mostly generated from the reaction of **5** with water rather than with the solvents or ligand backbone.

Scheme 1 Synthesis of boryllithium **5**.Fig. 1 Reference compounds [Dip = 2,6-(*i*-Pr)₂C₆H₃].

Structure of boryllithium

The DME-coordinated dimeric structure of boryllithium $[\mathbf{5}\text{-DME}]_2$ was confirmed by X-ray crystallographic analysis (Fig. 2). The solid-state structure of $[\mathbf{5}\text{-DME}]_2$ reveals a B–Li bond of 2.291(6) Å, which is 8.5 % longer than the sum of the covalent radii (2.11 Å) of boron and lithium atoms [51]. Structural comparison of $[\mathbf{5}\text{-DME}]_2$ with related compounds (Table 1) shows that the two B–N bond lengths [1.465(4) and 1.467(4) Å] in $[\mathbf{5}\text{-DME}]_2$ are longer than those [1.418(3) and 1.423(3) Å] in the hydroborane **6**, and that the angle of N1–B1–N2 [99.2(2)°] in $[\mathbf{5}\text{-DME}]_2$ is smaller than that in **6** [105.25(16)°]. These B–N lengths and the N–B–N angle in $[\mathbf{5}\text{-DME}]_2$ are closer to those in the previously calculated free boryl anion **8** (B–N = 1.475 Å; N–B–N = 97.72°) [42] than to those in **6**, consistent with a highly polarized B–Li bond and anionic character of the boron center in **5**. The structural change from **6** to $[\mathbf{5}\text{-DME}]_2$ is similar to that from the corresponding imidazolium salt **10** to singlet carbene **7** [52], reflecting the similar electronic character between $[\mathbf{5}\text{-DME}]_2$ and **7**.

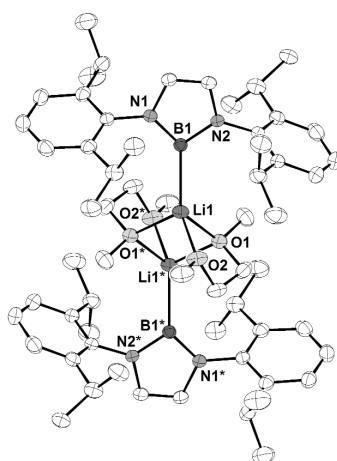
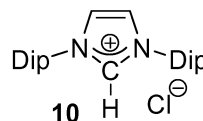


Fig. 2 Crystal structure of $[\mathbf{5}\text{-DME}]_2$ with 50 % thermal ellipsoids (hydrogen atoms and minor portions of disordered isopropyl groups were omitted for clarity).

Table 1 Structural comparison of boryllithium **5** with related compounds [Dip = 2,6-(*i*-Pr)₂C₆H₃].

compounds	6	$[\mathbf{5}\text{-DME}]_2$	8	10	7
B(or C)–N (Å)	1.418(3) 1.423(3)	1.465(4) 1.467(4)	1.475	1.341 1.338	1.364 1.369
N–B(or C)–N (°)	105.25(16)	99.2(2)	97.72	107.6	101.4
reference	this work	this work	42	52	52



Spectroscopic features of boryllithium

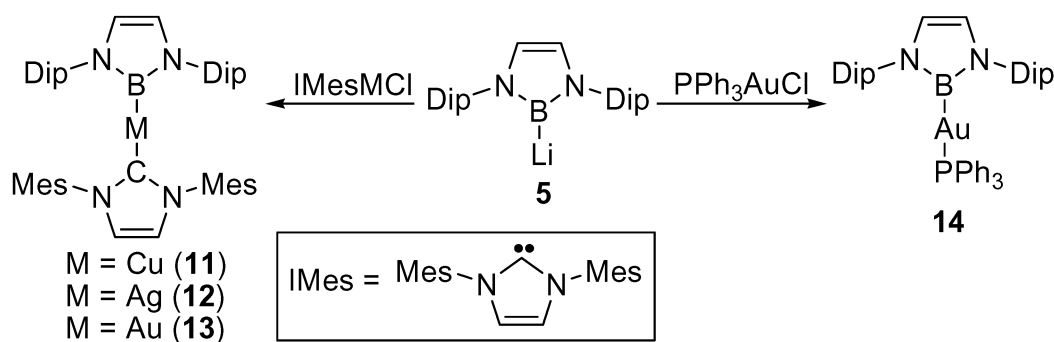
The boryllithium compound $[\mathbf{5}\text{-DME}]_2$ was also spectroscopically characterized in THF-*d*₈ solution. In the ¹H NMR spectrum of $[\mathbf{5}\text{-DME}]_2$ in THF-*d*₈, DME was found to dissociate from the lithium atom (free DME resonances were observed at 3.42 and 3.26 ppm). The ¹¹B NMR spectrum of **5** showed a resonance at 45.4 ppm with a large half-width of $h\nu_2 = 535$ Hz. The lower field shift and larger half-width of this signal relative to those of hydroborane **6** ($\delta_B = 22.9$ ppm, $h\nu_2 = 379$ Hz) can be attributed to the paramagnetic contribution to nuclear shielding by the low-lying transition from an sp² lone pair of the boryl anion to the π^* orbital on the dihydrodiazaborole ring, as was reported for the isoelectronic

singlet diaminocarbene [53]. Absence of splitting in the proton-coupled ^{11}B NMR spectrum of **5** confirmed that there is no B–H bond in **5**, whereas a ^{11}B – ^1H coupling constant of 154 Hz was detected for **6**. The ^7Li NMR spectrum of **5** showed a broad singlet signal with a peak at 0.46 ppm and a half-width of $h\nu_e = 36$ Hz; the large half-width may originate from the interaction of the lithium with the quadrupole boron nucleus [54]. Thus, the NMR spectroscopy of boryllithium **5** also indicates that the central boron atom has an anionic character with a highly polarized B–Li bond in solution.

A new methodology for the syntheses of boryl transition-metal complexes: Systematic study on the trans influence of boryl ligand

Syntheses of group 11 transition-metal boryl complexes

As many gallyl transition-metal complexes have been synthesized by nucleophilic introduction of anionic gallium species **9b** onto the transition-metal center [55–61], we also tried to the nucleophilic introduction of boryl ligand using boryl anion [62]. IMes–borylmetal complexes **11–13** [IMes = *N,N'*-bis(2,4,6-trimethylphenyl)-imidazole-2-ylidene] and PPh_3 –borylgold(I) complex **14** were synthesized through addition of **5** to equal amounts of IMes- or PPh_3 -ligated group 11 metal chlorides in THF (Scheme 2). All complexes were characterized by spectroscopic, elemental, and X-ray analyses and were shown to have a linear, two-coordinate structure (Fig. 3). Complexes **12–14** are the first examples of fully characterized borylsilver and borylgold complexes.



Scheme 2 Syntheses of group 11 borylmetal complexes with boryllithium **5** (yields of isolated product).

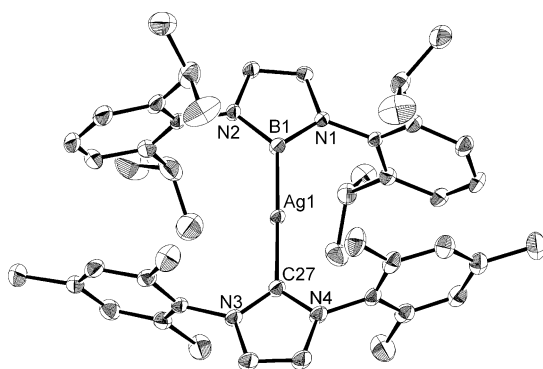


Fig. 3 Crystal structure of **12** with 50 % thermal ellipsoids (hydrogen atoms were omitted for clarity).

Structure of boryl complexes

Structural parameters of boryl complexes **11–14** are summarized in Table 2. In the borylcopper complex **11**, the Cu–B and Cu–C bond lengths are shorter than those in the recently isolated borylcopper complex **15** [Fig. 4.; 2.002(3) and 1.937(2) Å] [35]. Borylsilver complex **12** possesses two-center–two-electron (2c–2e) Ag–B bond that is shorter than the silver–boron interactions (2.35–2.76 Å) [63] in the previously reported hydroborane silver complexes, which have 3c–2e bonds consisting of boron, hydrogen, and silver atoms. Similarly, borylgold complexes **13** and **14** also have 2c–2e Au–B bond that is shorter than the gold–boron interactions (2.14–2.68 Å) [64] in cage compounds containing gold and boron atoms in which the boron atom forms one or more multicenter–multielectron bonds.

Table 2 Observed NMR chemical shifts of ^{11}B , ^{13}C (carbene), and ^{31}P nucleus, and selected bond lengths obtained from crystallographic data for **11–14** and reference compounds **16–20**.

Complexes	δ_{B}	δ_{C}	δ_{P}	M–B (Å)	M–C(P) (Å)
11	38.9	185.3		1.980(2)	1.918(2)
12	40.7	194.6		2.118(2)	2.1207(18)
13	45.1	217.0		2.074(4)	2.078(4)
14	45.4		57.7	2.076(6)	2.3469(13)
IMesAgCl (16)		184.0			2.056(7)
IMesAuCl (17)		173.4			1.998(5)
PPh ₃ AuCl (18)			33.5		2.235(3)
PPh ₃ AuPh (19)			44.0		2.296(2)
PPh ₃ AuMe (20)			47.7		2.279(8)

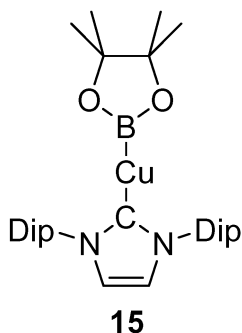


Fig. 4 Related borylcopper complex **15** [Dip = 2,6-(*i*-Pr)₂C₆H₃].

Trans influence of boryl ligand

The strong trans influence of a boryl ligand [65–67] is demonstrated by the following three features: (1) smaller silver–carbon coupling constants $^1J_{\text{C–Ag}}$ in **12** (81 and 88 Hz to ^{107}Ag and ^{109}Ag , respectively) than those in [IMesAgCl] (**16**; 234, 270 Hz) [68]; (2) the M–C_{carbene} bonds in **12** and **13** are longer than those of reference [IMesMCl] complexes **16** and **17** (M = Ag [68], Au [69]); and (3) the Au–P bonds in **14** are longer than those in a series of PPh₃–Au^I complexes **18–20** [70–72] that have an additional anionic ligand (Cl, Ph, or Me).

CONCLUSION

A boryl anion, boryllithium, has been synthesized and fully characterized. This novel species reacted with group 11 transition-metal chloride to form the corresponding boryl complexes.

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REFERENCES AND NOTES

1. B. J. Wakefield. *Organolithium Methods*, Academic Press, London (1988).
2. H. Nöth. In *Science of Synthesis*, D. E. Kaufmann, D. S. Matteson (Eds.), pp. 139–178, Georg Thieme Verlag, Stuttgart (2005).
3. R. W. Auten, C. A. Kraus. *J. Am. Chem. Soc.* **74**, 3398 (1952).
4. J. L. R. Williams, J. C. Doty, P. J. Grisdale, R. Searle, T. H. Regan, G. P. Happ, D. P. Maier. *J. Am. Chem. Soc.* **89**, 5153 (1967).
5. L. Weber, M. Schnieder, P. Lonneck. *J. Chem. Soc., Dalton Trans.* 3459 (2001).
6. R. Köster, G. Benedikt. *Angew. Chem., Int. Ed. Engl.* **2**, 219 (1963).
7. R. Köster, G. Benedikt. *Angew. Chem., Int. Ed. Engl.* **3**, 515 (1964).
8. K. Smith, K. Swaminathan. *J. Chem. Soc., Dalton Trans.* 2297 (1976).
9. J. D. Wilkey, G. B. Schuster. *J. Org. Chem.* **52**, 2117 (1987).
10. S. Boyatzis, J. D. Wilkey, G. B. Schuster. *J. Org. Chem.* **55**, 4537 (1990).
11. As examples of sp^3 boron anions, the existence of base-stabilized boryl anions ($\text{base-BH}_2^-\text{M}^+$, where base is amine or phosphine and R is *n*-Bu or H) was suggested as intermediates in reactions with electrophiles. See refs. [12–15]. Also, bishomotriborirane may be regarded as a boryl anion equivalent where the boron anion is electronically stabilized by a neighboring diboron unit to form an sp -hybridized boron atom. However, there is no B–Li bond in this molecule. See ref. [16].
12. T. D. Parsons, J. M. Self, L. H. Schaad. *J. Am. Chem. Soc.* **89**, 3446 (1967).
13. B. R. Gragg, G. E. Ryschkewitsch. *Inorg. Chem.* **15**, 1209 (1976).
14. A. Blumenthal, P. Bissinger, H. Schmidbaur. *J. Organomet. Chem.* **462**, 107 (1993).
15. T. Imamoto, T. Hikosaka. *J. Org. Chem.* **59**, 6753 (1994).
16. M. Unverzagt, G. Subramanian, M. Hofmann, P. V. Schleyer, S. Berger, K. Harms, W. Massa, A. Berndt. *Angew. Chem., Int. Ed. Engl.* **36**, 1469 (1997).
17. 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.* **98**, 2685 (1998).
18. H. Braunschweig. *Angew. Chem., Int. Ed.* **37**, 1786 (1998).
19. H. Braunschweig, M. Colling. *Coord. Chem. Rev.* **223**, 1 (2001).
20. H. Braunschweig, C. Kollann, D. Rais. *Angew. Chem., Int. Ed.* **45**, 5254 (2006).
21. M. R. Smith III. *Prog. Inorg. Chem.* **48**, 505 (1999).
22. S. Aldridge, D. L. Coombs. *Coord. Chem. Rev.* **248**, 535 (2004).

23. D. Männig, H. Nöth. *Angew. Chem., Int. Ed. Engl.* **24**, 878 (1985).
24. G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg, N. C. Norman. *Organometallics* **15**, 5137 (1996).
25. T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi, J. F. Hartwig. *J. Am. Chem. Soc.* **124**, 390 (2002).
26. K. M. Waltz, J. F. Hartwig. *J. Am. Chem. Soc.* **122**, 11358 (2000).
27. T. M. Boller, J. M. Murphy, M. Hapke, T. Ishiyama, N. Miyaura, J. F. Hartwig. *J. Am. Chem. Soc.* **127**, 14263 (2005).
28. S. A. Westcott, N. J. Taylor, T. B. Marder, R. T. Baker, N. J. Jones, J. C. Calabrese. *J. Chem. Soc. Chem. Commun.* 304 (1991).
29. R. T. Baker, J. C. Calabrese, S. A. Westcott, P. Nguyen, T. B. Marder. *J. Am. Chem. Soc.* **115**, 4367 (1993).
30. The first example of a boryl complex synthesized by salt elimination: (a) H. Nöth, G. Schmid. *Angew. Chem., Int. Ed. Engl.* **2**, 623 (1963); the first structurally characterized boryl complex made by salt elimination: (b) J. F. Hartwig, S. Huber. *J. Am. Chem. Soc.* **115**, 4908 (1993).
31. The first example of a boryl complex synthesized by oxidative addition: (a) G. Schmid, H. Nöth. *Z. Naturforsch. B* **20**, 1008 (1965); the first structurally characterized boryl complexes made by oxidative addition: (b) R. T. Baker, D. W. Ovenall, J. C. Calabrese, S. A. Westcott, N. J. Taylor, I. D. Williams, T. B. Marder. *J. Am. Chem. Soc.* **112**, 9399 (1990); (c) J. R. Knorr, J. S. Merola. *Organometallics* **9**, 3008 (1990).
32. Y. Kawano, T. Yasue, M. Shimoi. *J. Am. Chem. Soc.* **121**, 11744 (1999).
33. K. Takahashi, T. Ishiyama, N. Miyaura. *J. Organomet. Chem.* **625**, 47 (2001).
34. H. Ito, C. Kawakami, M. Sawamura. *J. Am. Chem. Soc.* **127**, 16034 (2005).
35. D. S. Laitar, P. Mueller, J. P. Sadighi. *J. Am. Chem. Soc.* **127**, 17196 (2005).
36. Y. Segawa, M. Yamashita, K. Nozaki. *Science* **314**, 113 (2006).
37. M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki. *J. Am. Chem. Soc.* **129**, 9570 (2007).
38. Y. Segawa, M. Yamashita, K. Nozaki. *Angew. Chem., Int. Ed.* **46**, 6710 (2007).
39. Theoretical calculation has indicated the diamino-boryllithium could be stable to isolate, see: M. Wagner, N. J. R. van Eikema Hommes, H. Nöth, P. v. R. Schleyer. *Inorg. Chem.* **34**, 607 (1995).
40. A. J. Arduengo, III, R. L. Harlow, M. Kline. *J. Am. Chem. Soc.* **113**, 361 (1991).
41. H.-W. Wanzlick. *Angew. Chem., Int. Ed. Engl.* **1**, 75 (1962).
42. N. Metzler-Nolte. *New J. Chem.* **22**, 793 (1998).
43. A. Sundermann, M. Reiher, W. W. Schoeller. *Eur. J. Inorg. Chem.* 305 (1998).
44. E. S. Schmidt, A. Jockisch, H. Schmidbaur. *J. Am. Chem. Soc.* **121**, 9758 (1999).
45. R. J. Baker, R. D. Farley, C. Jones, M. Kloth, D. M. Murphy. *J. Chem. Soc., Dalton Trans.* 3844 (2002).
46. R. J. Brotherton, A. L. McCloskey, L. L. Petterson, H. Steinberg. *J. Am. Chem. Soc.* **82**, 6242 (1960).
47. V. M. Dembitsky, H. Abu Ali, M. Srebnik. *Adv. Organomet. Chem.* **51**, 193 (2004).
48. T. B. Marder. In *Science of Synthesis*, D. E. Kaufmann, D. S. Matteson (Eds.), pp. 117–137, Georg Thieme Verlag, Stuttgart (2005).
49. M. B. Abrams, B. L. Scott, R. T. Baker. *Organometallics* **19**, 4944 (2000).
50. Hydroborane **6** was independently synthesized by a reduction of **4** with LiAlH₄ as was reported for the other *N*-heterocyclic hydroborane. See: L. Weber, E. Dobbert, H. G. Stämmler, B. Neumann, R. Boese, D. Blaser. *Eur. J. Inorg. Chem.* 491 (1999).
51. J. Emsley. *The Elements*, Oxford University Press, New York (1998).
52. A. J. Arduengo, III, R. Krafczyk, R. Schmutzler. *Tetrahedron* **55**, 14523 (1999).
53. A. J. Arduengo, D. A. Dixon, K. K. Kumashiro, C. Lee, W. P. Power, K. W. Zilm. *J. Am. Chem. Soc.* **116**, 6361 (1994).
54. N. P. Rath, T. P. Fehlner. *J. Am. Chem. Soc.* **110**, 5345 (1988).

55. R. J. Baker, C. Jones, J. A. Platts. *J. Am. Chem. Soc.* **125**, 10534 (2003).
56. R. J. Baker, C. Jones, J. A. Platts. *J. Chem. Soc., Dalton Trans.* 3673 (2003).
57. S. Aldridge, R. J. Baker, N. D. Coombs, C. Jones, R. P. Rose, A. Rossin, D. J. Willock. *J. Chem. Soc., Dalton Trans.* 3313 (2006).
58. P. L. Arnold, S. T. Liddle, J. McMaster, C. Jones, D. P. Mills. *J. Am. Chem. Soc.* **129**, 5360 (2007).
59. S. P. Green, C. Jones, D. P. Mills, A. Stasch. *Organometallics* **26**, 3424 (2007).
60. C. Jones, R. P. Rose, A. Stasch. *J. Chem. Soc., Dalton Trans.* 2997 (2007).
61. R. J. Baker, C. Jones. *Coord. Chem. Rev.* **249**, 1857 (2005).
62. Recently, Braunschweig indicated the possibility of a significant development in the area of metal boryl complexes using boryllithium, see: H. Braunschweig. *Angew. Chem., Int. Ed.* **46**, 1946 (2007).
63. The Cambridge Crystallographic Database showed 20 structures containing a B–Ag bond. In all of these complexes, B–Ag bonds can be considered as three-center–two-electron bonds with bridging hydrogen atoms. The shortest example of a B–Ag bond is 2.352(4) Å; see: H. M. Colquhoun, T. J. Greenhough, M. G. H. Wallbridge. *J. Chem. Soc., Chem. Commun.* 192 (1980).
64. The Cambridge Crystallographic Database showed 61 structures containing B–Au bond. In all of these complexes, the B–Au bonds can be considered as multicenter–multielectron bonds. The shortest example of a B–Au bond is 2.15(1) Å; see: A. J. C. Jeffery, P. A. Jelliss, F. G. A. Stone. *Organometallics* **13**, 2651 (1994).
65. H. Braunschweig, K. Radacki, D. Rais, D. Scheschkewitz. *Angew. Chem., Int. Ed.* **44**, 5651 (2005).
66. J. Zhu, Z. Y. Lin, T. B. Marder. *Inorg. Chem.* **44**, 9384 (2005).
67. H. Braunschweig, P. Brenner, A. Müller, K. Radacki, D. Rais, K. Uttinger. *Chem.—Eur. J.* **13**, 7171 (2007).
68. T. Ramnial, C. D. Abernethy, M. D. Spicer, I. D. McKenzie, I. D. Gay, J. A. C. Clyburne. *Inorg. Chem.* **42**, 1391 (2003).
69. P. de Fremont, N. M. Scott, E. D. Stevens, S. P. Nolan. *Organometallics* **24**, 2411 (2005).
70. N. C. Baenziger, W. E. Bennett, D. M. Soboroff. *Acta Crystallogr., Sect. B* **32**, 962 (1976).
71. P. D. Gavens, J. J. Guy, M. J. Mays, G. M. Sheldrick. *Acta Crystallogr., Sect. B* **33**, 137 (1977).
72. X. Hong, K. K. Cheung, C. X. Guo, C. M. Che. *J. Chem. Soc., Dalton Trans.* 1867 (1994).