Boryl Anions

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Syntheses, Structures, and Reactivities of Borylcopper and -zinc Compounds: 1,4-Silaboration of an α,β-Unsaturated Ketone to Form a γ-Siloxyallylborane**

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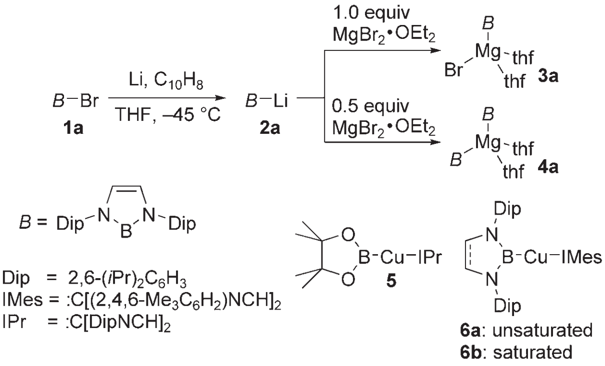
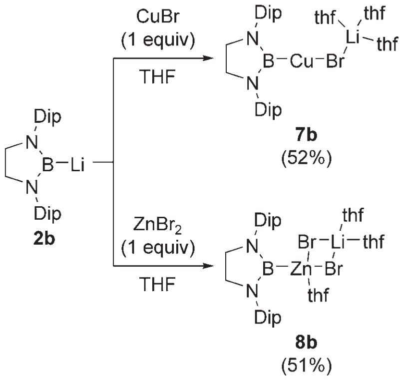
Carbanions are one of the most important reagents in synthetic organic chemistry.[1] They act as a carbon nucleophile to form a carbon–carbon bond as a consequence of the highly polarized carbon–metal bonds ($C^{\delta-}{-}M^{\delta+}$). The properties of polar carbon–metal bonds in a carbanionic species depend on the metallic counterpart, such as lithium, magnesium, copper, and zinc. The first two organometallic compounds directly attack the carbonyl group of α,β-unsaturated ketones, whereas the latter two[2] react by 1,4-addition (conjugate addition).[3]

In contrast to the rich chemistry of carbanions, there is a limited number of examples of boryl anions. We recently reported the first synthesis of boryllithium **2a** as a boron nucleophile.[4] Borylmagnesium species **3a** and **4a** could be synthesized by transmetalation reactions of **2a** with magnesium bromide, and behave as nucleophiles.[5] Prior to our recent studies on boryllithium and borylmagnesium compounds, there have been reports proposing a formation of a nucleophilic borylcopper intermediate that reacts with organic electrophiles, such as α,β-unsaturated carbonyls[6] or allylic esters.[7] Recently, a borylcopper species (**5**) was isolated[8] and its reactivity as a nucleophile toward carbonyl compounds has been studied experimentally[8,9] and theoretically.[10] Our recent study on a nucleophilic borylation using boryllithium to form a series of boryl–Group 11 metal complexes also resulted in the isolation of borylcopper species **6a**,**b**.[11] Although borylcopper species **5** and **6a**,**b** having an N-heterocyclic carbene ligand were isolated, there have been no reports with copper having boryl ligands instead of carbyl ligands as in a conventional organocopper, $[(RCu)_n]$, or Gilman-type cuprates, $[R_2CuLi]$. Borylzinc species possessing boron–zinc two-center, two-electron bonds have also not yet been synthesized.[12] To develop the chemistry of boryl anions, it is also important to estimate the properties of borylcopper and borylzinc compounds which have a conventional formula as with carbanionic species, because they may show different reactivities with organic electrophiles compared with those observed for boryllithium and borylmagnesium compounds.



Herein, we report the syntheses and structures of borylcopper and borylzinc compounds, and their reactivity with α,β-unsaturated ketones as boryl anions, where trapping of the enolate intermediate with silyl electrophile gives the corresponding 1,4-silaboration product, γ-siloxyallylborane.

Transmetalation of boryllithium **2b**, which was prepared from bromoborane **1b**,[11] with one equivalent of CuBr and $ZnBr_2$, respectively, followed by recrystallization of the products from pentane, gave crystals of lithium borylbromocuprate **7b** and lithium boryldibromozincate **8b** (Scheme 1). The two "ate" complexes **7b** and **8b** were spectroscopically



Scheme 1. Syntheses and yields of **7b** and **8b** by transmetalation of boryllithium **2b**. Dip = 2,6-diisopropylphenyl.

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and structurally characterized. The ^{11}B NMR spectrum has a broad signal at 45 ppm for **7b**, and at 41 ppm for **8b**. These values are comparable to that of boryllithium **2b** (52 ppm). The molecular structures of **7b** and **8b** were determined by X-ray structural analysis (Figure 1 and 2).[13] The first example of a borylcuprate, **7b**, contains a B-Cu-Br-Li chain with three tetrahydrofuran molecules coordinating to the lithium atom.[14] The average B–Cu bond length of **7b** (1.983 Å) is similar to that of carbene borylcopper complex **6b** (1.983(3) Å),[11] and somewhat shorter than that of **5** (2.002(3) Å).[8] The average B-Cu-Br angle of **7b** (172.0°) is slightly bent, as was observed for the B-Cu-C angle of **5** (168.07(16)°),[8] whereas that of **6b** was almost linear (179.41(15)°).[11] This difference may arise from the less-bulky bridging bromide ligand on the central copper atom in **7b** compared to carbene ligand in **6b**. Lithium boryldibromozincate **8b**[15] is the first example containing a two-center, two-electron B–Zn bond, and the B–Zn bond length (2.075(5) Å) is slightly shorter[16] than the sum of covalent radii (2.13 Å)[17] of boron and zinc atoms, and than the shortest B–Zn bond length (2.15(2) Å)[12d] among the previously reported multicenter, multielectron B–Zn bonds.[12]

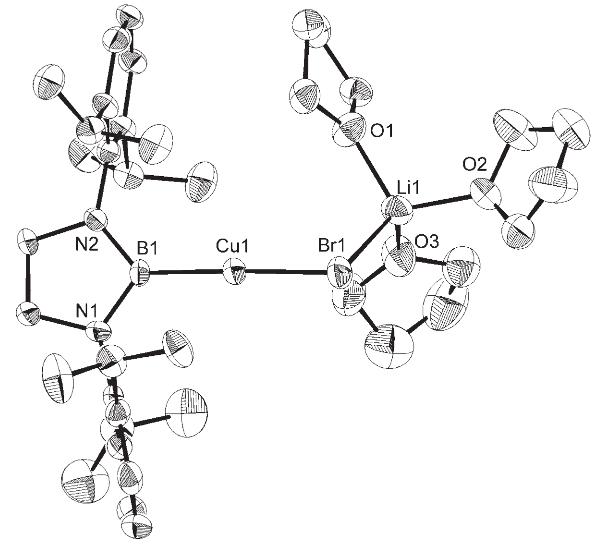


Figure 1. ORTEP drawing one of two independent molecules of **7b**, with ellipsoids set at 50% probability. Hydrogen atoms and minor contributors to disordered THF molecules are omitted for clarity.

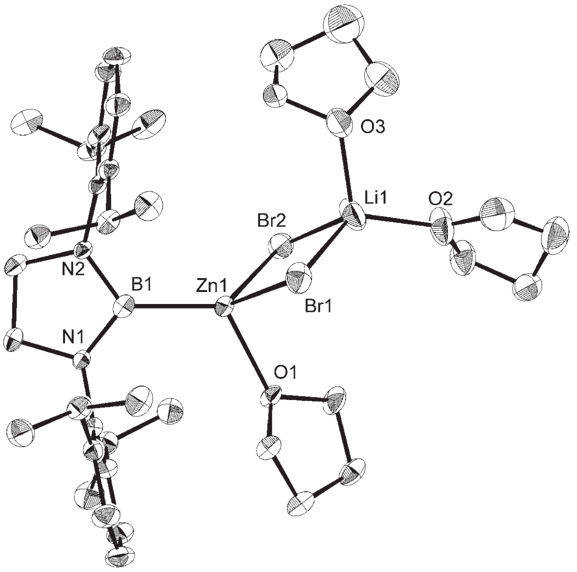
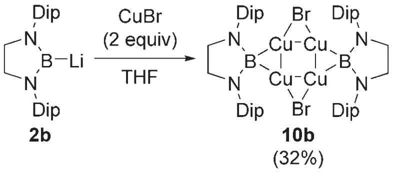


Figure 2. ORTEP drawing of **8b**, with ellipsoids set at 50% probability. Hydrogen atoms and minor contributors to disordered THF molecules are omitted for clarity.

Tetranuclear copper(I) complex **10b** was formed by changing the stoichiometry of CuBr to boryllithium **2b** to 2:1 (Scheme 2). The ^{11}B NMR spectrum of **10b** has a broad signal at 38 ppm, which is shifted slightly upfield compared to that of **7b** (45 ppm). The structure of **10b** obtained from crystallographic analysis is shown in Figure 3.[18] Each of the two bromine atoms and two boron atoms bridges two copper atoms in an alternating fashion.[19] The B–Cu bond lengths in **10b** (2.093(4) and 2.073(5) Å) are longer than the two-center, two-electron bonds in **7b**, which may reflect a bridging situation of the boryl ligand, as was observed for previously reported bridging boryl complexes.[20]



Scheme 2. Synthesis and yield of tetranuclear copper complex **10b**.

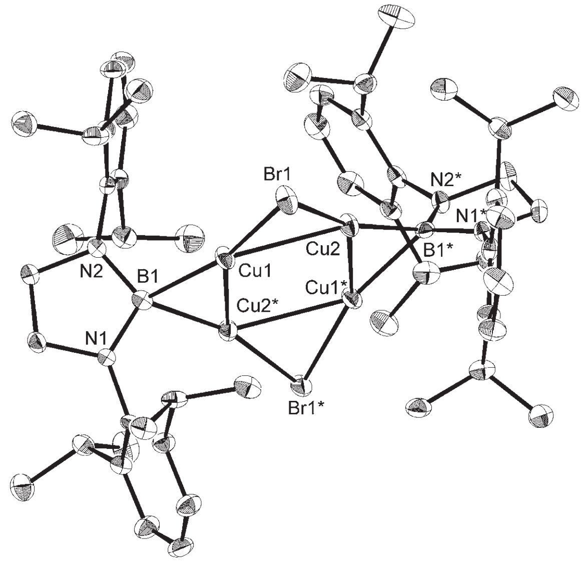
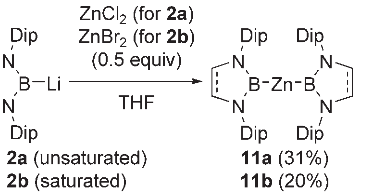


Figure 3. ORTEP drawing of **10b**, with ellipsoids set at 50% probability. Hydrogen atoms and minor contributors to disordered bromine atoms are omitted for clarity. One half of the whole molecule is an asymmetric unit.

Solvent-free diborylzinc species **11a** and **11b** were obtained as colorless, crystalline solids by addition of 0.5 equivalents of zinc halide to boryllithium compounds **2a** and **2b**, respectively (Scheme 3). The ^{11}B NMR spectrum has a broad signal at 32 ppm for **11a**, and at 38 ppm for **11b**. The ^{1}H and ^{13}C NMR signals of **11** were slightly shifted from those of recently reported diborylmagnesium species.[5] X-ray crystallographic analysis (Figure 4 for **11a**; see the Supporting Information for **11b**) revealed that diborylzinc compounds **11a** and **11b** have a two-coordinate linear structure[21] in which the B-Zn-B angles are 178.50(11)° for **11a** and 177.41(11)° for **11b**, as reported for most dialkylzinc and diarylzinc species.[22] It should be noted that **11a** and **11b** are the first isolated examples of a homoleptic borylmetal species.[23] The B–Zn bond distances (2.052(3) and 2.053(3) Å for **11a**) are slightly shorter than that in boryldibromozincate **8b** (2.075(5) Å). Saturation of the C–C bond in the boron-containing five-membered ring leads to a longer B–Zn bond (2.088(3) and 2.087(3) Å for **11b**).[24]



Scheme 3. Syntheses and yields of diborylzinc complexes **11a** and **11b**.

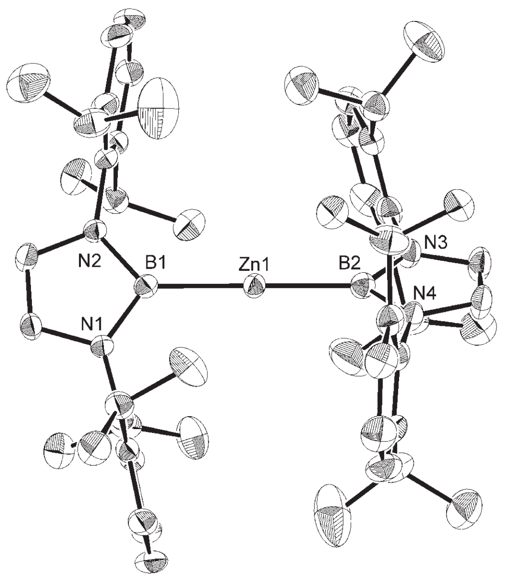
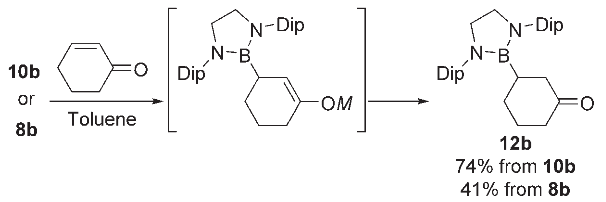
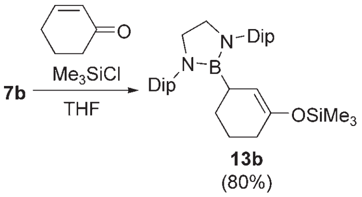


Figure 4. ORTEP drawing of **11a**, with ellipsoids set at 50% probability. Hydrogen atoms and minor contributors to disordered isopropyl groups are omitted for clarity.

To investigate the reactivity of the boryl compounds as boron nucleophiles, borylcopper **10b** and borylzinc **8b** were allowed to react with an α,β-unsaturated ketone. Thus, the reaction of **10b** or **8b** with 2-cyclohexen-1-one gave the corresponding conjugate addition product, 3-borylcyclohexan-1-one **12b**, in 74 and 41% yield after hydrolysis (Scheme 4). In the case of **8b**, the lithium atom is expected to act as a Lewis acid to achieve the conjugate addition.[25] In contrast, the reaction of boryllithium **2b** with 2-cyclohexen-1-one led only to protonation of **2b** (as detected by ^{1}H NMR spectroscopy) to form the corresponding hydroborane [HB(NDipCH$_2$)$_2$] (**14**) instead of the 1,2- or 1,4-addition product. The β-borylketone **12b** was characterized by X-ray crystallography (see the Supporting Information), and the formation of the C–B bond was also confirmed by ^{13}C NMR spectroscopy, which showed a broad signal ($\delta = 25.23$) arising from coupling to the quadrupolar ^{11}B nucleus. The regioselectivity of the addition is the same as those of organocuprates,[2a,b] organozincates,[3] and transient borylcopper species.[6] Trapping the copper enolate intermediate generated from **7b** and 2-cyclohexen-1-one with Me$_3$SiCl afforded γ-siloxyallylborane **13b** in 80% yield (Scheme 5). The γ-siloxyallylborane **13b** is both a silicon enolate and an allylborane. Multistep syntheses of such γ-siloxyallylboranes and their application to organic synthesis have been reported.[26] It should be noted that transition-metal-catalyzed silaboration of an α,β-unsaturated ketone affords complementary products, presumably arising from the γ-boroxyallylsilane.[27] Thus, it is not completely clear whether the γ-boroxyallylsilane is actually formed prior to hydrolysis in Oestereich's system.



Scheme 4. Reaction of **8b** or **10b** with 2-cyclohexen-1-one. *M* denotes {CuL$_n$} (from **10b**) or {ZnL$_n$} (from **8b**) where L = Br, LiBr, or thf.



Scheme 5. Synthesis of γ-siloxyallylborane **13b** from **7b**.

In summary, a series of new borylmetal species, namely the borylcopper compounds **7b** and **10b** and borylzinc compounds **8b** and **11a,b**, were synthesized by a transmetalation reaction of boryllithium with metal halides, and were structurally characterized by X-ray crystallography. Tetranuclear borylcopper **10b** and borylzincate **8b** reacted with 2-cyclohexen-1-one to form the corresponding conjugate addition product **12b**. Trapping the borylated copper enolate generated from **7b** and 2-cyclohexen-1-one with Me$_3$SiCl afforded γ-siloxyallylborane **13b**. Further investigations on the reactivity of these boryl metal compounds and the application of **12b** and **13b** to synthetic organic chemistry are currently in progress.

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[3] Compared to the Gilman diorganocuprate, LiCuR$_2$, 1,4-addition of organozinc reagents is relatively rare. However, triorganozincate species have been known to undergo 1,4-addition to α,β-unsaturated carbonyl compounds: See a) M. Isobe, S. Kondo, N. Nagasawa, T. Goto, *Chem. Lett.* **1977**, 679–682; b) J. F. G. A. Jansen, B. L. Feringa, *Tetrahedron Lett.* **1988**, *29*, 3593–3596; c) W. Tückmantel, K. Oshima, H. Nozaki, *Chem. Ber.* **1986**, *119*, 1581–1593; d) R. A. Kjonaas, R. K. Hoffer, *J. Org. Chem.* **1988**, *53*, 4133–4135; e) M. Uchiyama, M. Kameda, O. Mishima, N. Yokoyama, M. Koike, Y. Kondo, T. Sakamoto, *J. Am. Chem. Soc.* **1998**, *120*, 4934–4946; f) M. Uchiyama, S. Nakamura, T. Furuyama, E. Nakamura, K. Morokuma, *J. Am. Chem. Soc.* **2007**, *129*, 13360–13361.

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[13] Crystal data and a summary of the intensity data collection parameters for **7b**, **8b**, **10b**, **11a**, **11b**, and **12b** are listed in Table S1 of the Supporting Information. In each case, a suitable crystal was mounted with cooled mineral oil on a glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) to $2\theta_{\max} = 55°$. The structures were solved by direct methods with SIR-97 (A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119) and refined by full-matrix least-squares techniques against F^2 SHELXL-97 (G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, **1997**) The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically in the difference Fourier maps or placed using AFIX instructions. CCDC-668896 (**7b**), CCDC-668897 (**8b**), CCDC-668898 (**10b**), CCDC-675171 (**11a**), CCDC-680348 (**11b**), and CCDC-668899 (**12b**) 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.

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[15] A related lithium alkyldibromozincate, [{(PhN(Me)Me$_2$Si)-(Me$_3$Si)$_2$C}-Zn(μ^2-Br)$_2$Li(thf)$_2$] (**9**), has also been structurally characterized, and has a C−Zn bond length of 2.014(5) Å, which is similar to the sum of covalent radii (2.02 Å) of the carbon and zinc atoms. See D. Azarifar, M. P. Coles, S. M. El-Hamruni, C. Eaborn, P. B. Hitchcock, J. D. Smith, *J. Organomet. Chem.* **2004**, *689*, 1718–1722. On the other hand, the average length of the Zn−(μ^2-Br) bonds in **8b** (2.504 Å) are longer than those in **9** (2.4217 Å), probably because of the coordination of THF molecules to the zinc atom in **8b**.

[16] This is in contrast to boryllithium **2a**[4] and borylmagnesium compounds **3** and **4**,[5] in which the B−M bond (M = Li or Mg) is longer than the sum of covalent radii, probably owing to the difference in polarity of boron−metal bond.

[17] J. Emsley, *The Elements*, 3rd ed., Oxford University Press, New York, **1998**.

[18] The Cu−Cu distances of **10b** are 2.3120(11) Å for boron-bridged moiety and 2.6504(12) Å for bromine-bridged unit. The former is shorter than those of tetranuclear mesitylcopper [(MesCu)$_4$]·(thf)$_4$ (2.414(2) and 2.432(2) Å; See, H. Eriksson, M. Håkansson, *Organometallics* **1997**, *16*, 4243–4244), probably owing to the existence of an electronegative bromine atom, which makes the

B–Cu interaction stronger than the C–Cu interaction in tetranuclear mesitylcopper species, even though the boron atom is larger than carbon.

[19] In contrast to **10b**, a related tetranuclear copper complex possessing two aryl groups and two bromine atoms has been structurally characterized in which two bridging bromide ions share one copper atom of a Cu_4 core. See M. D. Janssen, M. A. Corsten, A. L. Spek, D. M. Grove, G. van Koten, *Organometallics* **1996**, *15*, 2810–2820.

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[21] The linear structures of **11a** and **11b** is in contrast to that of diphenylzinc, which has a dimeric structure containing a C-Zn-C-Zn core with bridging phenyl ligands. See P. R. Markies, G. Schat, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets, A. L. Spek, *Organometallics* **1990**, *9*, 2243–2247.

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