

Design, Generation, and Synthetic Application of Borylzincate: Borylation of Aryl Halides and Borylzincation of Benzyne/Terminal Alkyne

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S Supporting Information

ABSTRACT: Borylzincate was generated *in situ* from dialkylzinc, diboron, and metal alkoxide. Model DFT calculations showed that although the formation of borylzincate is kinetically favorable, it is thermodynamically unfavorable. Therefore, we designed a successive reaction sequence that would provide a compensating energy gain. This enabled Zn-catalyzed borylation of aryl halides and borylzincation of benzyne and terminal alkyne from diborons without the need for any cocatalyst.

Organozincate compounds have opened new avenues in organic and organometallic chemistry.¹ Recently, increasing attention has been devoted to heteroelement (heteroleptic) zincates, in addition to the large body of homoleptic alkylzincates, because of their unique reactivities and selectivities.^{2–4} For example, dialkylhydride zincate complexes, which can be readily prepared from dialkylzinc and NaH or LiH, act as efficient hydride reductants for carbonyl compounds.² Dialkylamidozincates and dianionic silylzincates promote directed *ortho*-zincation of a wide range of (hetero)aromatics³ and regioselective silylzincation of terminal alkynes without any transition metal catalyst,⁴ respectively. Borylzincates are also potentially attractive as novel functional zincates and synthetic tools.⁵ However, boryl anions have been regarded as difficult to generate, with a few sophisticated exceptions,⁶ such as a finely stabilized borylanion reported by Yamashita, Nozaki et al.⁷ and the borylcopper–NHC complex reported by Sadighi et al.^{8,9} However, all of our model calculations implied that the generation of borylzincate species is not so difficult (activation barriers <20 kcal/mol), and the key issue appears to be overcoming the rather large endothermicity (>10 kcal/mol, Figure 1).¹⁰ Thus, we speculated that borylzincate species could be useful in organic synthesis if the unfavorable energy loss could be compensated by successive reaction(s). We disclose here the *in situ* generation of borylzincate complexes from diborons via B–B bond cleavage, which enables some unprecedented and highly chemoselective borylation reactions.

First, we envisioned the catalytic borylation reaction of aryl halides^{9,11,12} via a halogen–zinc exchange reaction with *in situ* generated borylzincate species A (Scheme 1) to afford the corresponding arylzincate B and boryl halide C, a potent electrophile, which results in the formation of arylboronate D

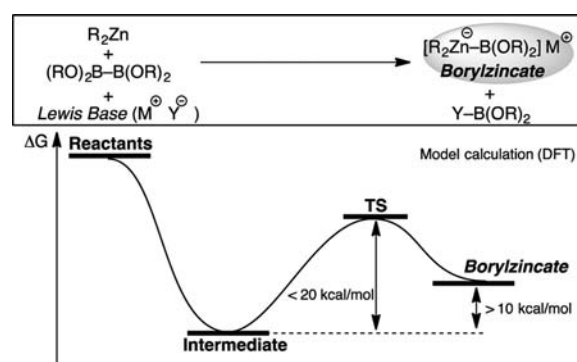
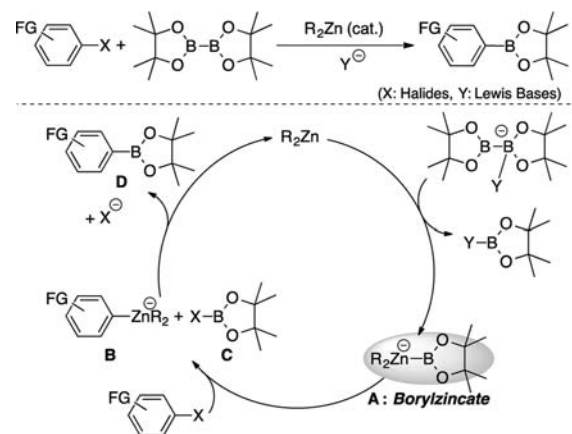


Figure 1. Energy profile for generation of borylzincate species from diboron, Lewis base, and dialkylzinc.

Scheme 1. Proposed Borylation Reaction Mechanism



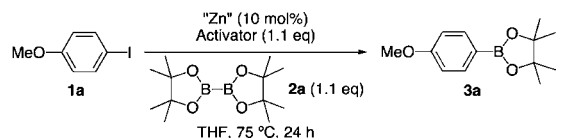
and regeneration of dialkylzinc. The energy gain is a result of the formation of the stable C–B bond in D from the unstable B–Zn bond in A in the reaction sequence.

We commenced our “proof of concept” by exploring the borylation of 4-iodoanisole (1a) with bis(pinacolato)diboron (2a) in the presence of a catalytic amount of diethylzinc (10 mol %) and various Lewis base “activators” (1.1 equiv) in THF at 75 °C (Table 1). In the absence of activator, only a trace amount of

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Table 1. Optimization of Conditions



| Entry | Activator | "Zn" | Yield (%) ^a | Entry ^d | Activator | "Zn" | Yield (%) ^a |
|-------|---------------------|--------------------|------------------------|--------------------|------------------------------------|--------------------|------------------------|
| 1 | none | Et ₂ Zn | trace | 8 | LiO ^t Bu | Et ₂ Zn | 63 |
| 2 | LiF | ↓ | trace | 9 | KO ^t Bu | ↓ | 51 |
| 3 | NaF | ↓ | 23 | 10 | Mg(O ^t Bu) ₂ | ↓ | 69 |
| 4 | KF | ↓ | 57 | 11 | Ca(OEt) ₂ | ↓ | 53 |
| 5 | CsF | ↓ | 50 | 12 | NaO ^t Bu | Me ₂ Zn | 72 |
| 6 | NaOMe | ↓ | 58 | 13 | ↓ | ZnCl ₂ | 0 |
| 7 | NaO ^t Bu | ↓ | 82 | 14 | ↓ | none | 0 |

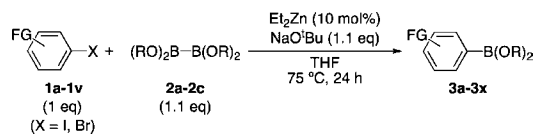
^aNMR yield determined by ¹H NMR analysis.

the desired product was obtained (entry 1). The use of fluoride anion promoted the reaction moderately (entries 2–5). When alkoxide anion was employed as an activator, the starting iodoarene **1a** was completely consumed. The use of NaO^tBu gave **3a** in excellent yield (82%, entry 7). Other metal alkoxides among those examined did not improve the reaction outcome (entries 8–11). The chemical yield was slightly decreased (72%) with Me₂Zn (entry 12), and no product formation was observed with ZnCl₂ (entry 13). The formation of borylzincate is essential for this catalytic borylation; the yield of the product **3a** was <1% when R₂Zn was omitted (entry 14).¹³

With the optimized conditions in hand, we examined the scope of the present borylation, as summarized in Table 2. Iodobenzene and its derivatives substituted with electron-donating groups, including methoxy and methyl groups, were efficiently converted to the corresponding boronates **3a–f** (entries 1–6). In particular, the substituent position (*ortho*, *meta*, or *para*) of the methoxy group had no effect on the reaction (entries 1–3), and some sterically demanding substrates reacted without difficulty (entries 3, 5, 15, and 21). Electron-withdrawing substituents, such as CF₃, halogens, amide, ester, and CN groups, which are sensitive to base or metal reagents, are compatible with the present borylation reaction, affording the corresponding boronates in good to excellent yield (entries 7–14). Besides aryl iodides, aryl bromides can be utilized at higher temperature (120 °C) (entries 1, 3, 7, and 20), and **3j** was the sole product (75% yield) from the reaction of 4-bromo-iodobenzene at 75 °C (entry 10). Other types of aryl iodides, including naphthyl and a variety of heteroaromatics, were applicable (entries 15–20). Substrates having an allyloxy group at an *ortho* or *para* position afforded the desired products in good yield (entries 21 and 22). These results clearly suggest the utility of the Zn-catalyzed borylation, since these substrates are not compatible with Pd-catalyzed borylation.^{11,12a} Moreover, the results of entry 21 provided some mechanistic insight; i.e., the radical mechanism is not plausible, since the *5-exo-trig* cyclization byproduct was not detected at all.¹³ To our knowledge, this reaction is the first example of an ionic borylation of aryl halides using diborons without any transition metal catalysts.

The structural requirement of diboron was also examined. Using bis(catecholato)diboron (**2b**) and bis(neopentylglycolato)diboron (**2c**), the corresponding aryl boronates **3w** and **3x** were obtained in 72% and 64% yield, respectively (entries 23 and 24). Thus, the present Zn-catalyzed borylation has a broad substrate generality.

Table 2. Zn-Catalyzed Borylation of Aryl Halides



| Entry | Product | Yield (%) ^a | Entry | Product | Yield (%) ^a |
|-------|-----------|------------------------|-------|-----------|------------------------|
| 1 | 3a | 82 83 ^c | 13 | 3m | 65 |
| 2 | 3b | 91 | 14 | 3n | 60 |
| 3 | 3c | 86 83 ^c | 15 | 3o | 93 |
| 4 | 3d | 86 | 16 | 3p | 72 ^d |
| 5 | 3e | 80 ^d | 17 | 3q | 76 |
| 6 | 3f | 85 | 18 | 3r | 74 |
| 7 | 3g | 92 95 ^c | 19 | 3s | 80 |
| 8 | 3h | quant. | 20 | 3t | 95 93 ^c |
| 9 | 3i | 92 | 21 | 3u | 71(77 ^b) |
| 10 | 3j | 75 | 22 | 3v | 60 |
| 11 | 3k | 83 | 23 | 3w | 72 ^d |
| 12 | 3l | 63(74 ^b) | 24 | 3x | 64 |

Bis(pinacolato)diboron **2a** (entries 1–22), bis(catecholato)diboron **2b** (entry 23), and bis(neopentylglycolato)diboron **2c** (entry 24) were used as diborons **2**. ^aIsolated yield. ^bNMR yield determined by ¹H NMR analysis. ^cIsolated yield using aryl bromides instead of aryl iodides as starting materials **1**, with heating to 120 °C. ^dIsolated yield, with heating to 120 °C.

DFT model calculations provide a clear rationale for the proposed mechanism of the borylzincate-mediated ionic borylation of aryl halides. The calculated potential energy profiles are summarized in Figure 2. The primary role of borylzincate is to stabilize the pre-reaction intermediate and the halogen–zinc exchange TS by cooperative synergy of the counteraction, Me₂Zn, and [−]B(OR)₂ moiety (see Supporting Information for details). Also noteworthy is that the successive reaction sequence provides a large energy gain (26.6 + 50.0 kcal/mol) to regenerate dialkylzinc for the next catalytic cycle. Thus, the zincate serves to mediate boron transfer through the two IMs/TSs.

Next, we examined the borylzincation of unsaturated bonds with the *in situ*-generated borylzincate species. Benzynes was

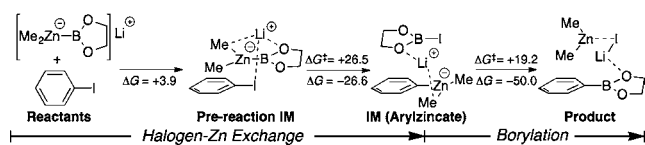


Figure 2. Energy profile for borylzincate-mediated ionic borylation of aryl iodides (B3LYP/LANL2DZ for I, SVP for Zn, and 6-31+G* for others; energy in kcal/mol).

selected as the first substrate,¹⁴ because the relief of strain of the “unstable” triple bond of benzyne should provide a large energy gain in the borylzincation process (Figure 1). When benzyne, prepared from (2-trimethylsilyl)phenyl trifluoromethanesulfonate (**4k**) with KF/18-crown-6,¹⁵ was treated with diethylzinc, **2a**, and KF, followed by quenching with H₂O, the borylated product **3f** was obtained in 66% yield (eq 1, bottom of Table 3). The reaction did not proceed at all in the absence of Et₂Zn,¹⁶ supporting the idea that borylzincation of benzyne occurs via *in situ* generation of borylzincate species.

One of our group previously reported another benzyne formation reaction of *o*-halo-iodobenzene derivatives using trialkylzincate, which provided a chemoselective and regio-controlled method for generation of functionalized benzyne.^{3b} In addition, silylzincation of the generated substituted benzyne to give a multifunctionalized zincate, (*o*-silylaryl)zincate species, was achieved using a silylzincate, Me₂Zn(SiMe₂Ph)Li, prepared from Me₂Zn and Me₂PhSiLi.^{3d} We therefore investigated similar borylzincations of functionalized benzyne (Table 3). After intensive screening of activators, Mg(O^tBu)₂ was found to be the best.¹⁷ The reaction of 2-bromoiodobenzene (**4a**) provided the 2-borylphenylzincate species, which reacted with allyl bromide to afford (2-allylphenyl)boronic acid pinacol ester **5a** in 84% yield. The use of **4b** or **4c** caused no problems (entries 2 and 3), and trapping of the generated arylzincate with I₂ gave the desired product in good yield (78%, entry 4). 3-Substituted benzyne were also examined, in the expectation of obtaining 1,2,3-trisubstituted benzene derivatives. When 2-iodo-3-bromoanisole (**4d**) was used under the optimized conditions, **3b** was exclusively obtained in 84% yield after quenching with H₂O (entry 5). Trapping with allyl bromide or I₂ also gave the desired multifunctionalized benzene in a highly regioselective manner (entries 6 and 7). In addition to the methoxy group, other directing groups, such as F, Cl, and CN, induced highly selective borylzincation, affording the corresponding products after electrophilic trapping (entries 8–13). 4-Fluoro- and 4-methyl-2-iodobromobenzene (**4j** and **4k**) gave the borylated products as mixtures of regioisomers (1:2.6 and 1:1.1, respectively, entries 14 and 15). In other words, the low selectivity with these substrates reflects the fact that benzyne formation was involved prior to the borylzincation.

The present borylzincation was finally applied to a terminal alkyne (Scheme 2).¹⁸ Phenylacetylene (**6**) was treated under conditions similar to those used for benzyne, and after electrophilic trapping with H₂O, the borylated product was obtained in moderate (51%) yield, presumably reflecting the fact that reactivity of the C–C triple bond of **6** is lower than that of benzyne.

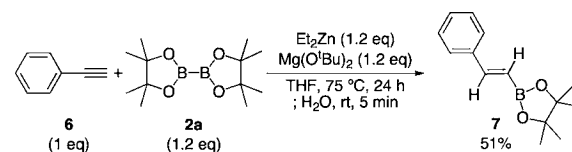
In summary, we have developed a method for *in situ* generation of borylzincate species using dialkylzinc and diboron activated by Lewis basic metal alkoxide. Calculations suggested that the formation of borylzincate would be thermodynamically unfavorable, but this could be overcome by designing the overall reaction sequence so that the subsequent step provides a

Table 3. Borylzincation of Benzyne

| Entry | Substrate | E ^c | Product | Yield (%) ^a |
|-----------------|---------------------|--|-----------------------|-------------------------|
| 1 | 4a (X = Br) | allyl bromide | 5a | 84 |
| 2 | 4b (X = I) | | | 81 |
| 3 | 4c (X = OTf) | | | 63 |
| 4 | 4a | I ₂ | 5b | 78 |
| 5 | 4d | H ₂ O | 3b (E = H) | 84 |
| 6 | | allyl bromide | 5c (E = allyl) | 56(77 ^b) |
| 7 | | I ₂ | 5d (E = I) | 44(71 ^b) |
| 8 ^d | 4e | H ₂ O | 3h (E = H) | 73 |
| 9 ^d | | allyl bromide | 5e (E = allyl) | 51 |
| 10 ^d | | I ₂ | 5f (E = I) | 49(66 ^b) |
| 11 ^d | 4f | H ₂ O | 5g (E = H) | 82 |
| 12 ^d | | allyl bromide | 5h (E = allyl) | 58(72 ^b) |
| 13 ^d | 4g | H ₂ O | 5i | 76 |
| 14 | 4i | H ₂ O | 3h (meta) | 83 |
| | | | 5j (para) | (3h:5j = 1:2.6) |
| 15 | 4j | H ₂ O | 3e (meta) | 63 |
| | | | 5k (para) | (3e:5k = 1:1.1) |
| | 4k (1 eq) | Et ₂ Zn (1.1 eq) KF (2 eq) 18-crown-6 (1 eq) THF, 70 °C, 24 h ; H ₂ O (excess) | 3f | 66% ^a |

^aIsolated yield. ^bYield determined by ¹H NMR analysis. ^cThe reactions with electrophiles were carried at room temperature with H₂O for 5 min or with I₂ for 3 h, or at 75 °C with allyl bromide for 12 h. ^dThe amount of **2a** was 3 equiv.

Scheme 2. Borylzincation of Terminal Alkyne



compensating energy gain. This method enables borylation of aryl halides with broad substrate generality. The high nucleophilicity of the boryl ligand in borylzincate was crucial for efficient halogen–zinc exchange reaction and for catalytic use of dialkylzinc. Regioselective borylzincation of benzyne was also achieved under similar conditions, affording multifunctionalized aromatic compounds. We believe that a successive reaction approach utilizing *in situ*-generated unstable and highly reactive species is a powerful strategy with potentially broad applicability for developing further functions of zincates. Efforts to apply this approach to a variety of reactions and to elucidate the present

reaction pathway/mechanism with the help of theoretical and spectroscopic studies are in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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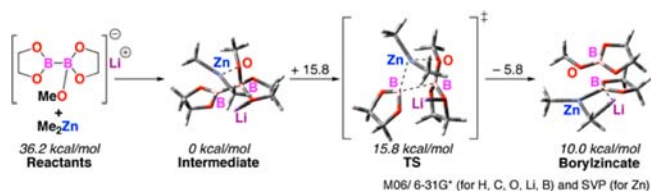
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(10) For example, DFT analysis of a possible pathway for generation of borylzincate species from bis(ethyleneglycolato)diboron, LiOMe, and Me₂Zn as model substrates is depicted below:



(11) Borylations of aryl halides using diborons catalyzed by transition metal catalysts have been reported. For Pd-catalyzed reactions, see: (a) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508. (b) Ishiyama, T.; Itoh, Y.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1997**, *38*, 3447. (c) Ishiyama, T.; Ishida, K.; Miyaura, N. *Tetrahedron* **2001**, *57*, 9813. (d) Zhu, L.; Duquette, J.; Zhang, M. *J. Org. Chem.* **2003**, *68*, 3729. (e) Fürstner, A.; Seidel, G. *Org. Lett.* **2002**, *4*, 541. (f) Billingsley, K. L.; Barder, T. E.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 5359. (g) Molander, G. A.; Trice, S. L. J.; Dreher, S. D. *J. Am. Chem. Soc.* **2010**, *132*, 17701. (h) Kawamorita, S.; Ohmiya, H.; Iwai, T.; Sawamura, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 8363. (i) Tang, W.; Keshipeddy, S.; Zhang, Y.; Wei, X.; Savoie, J.; Patel, N. D.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2011**, *13*, 1366. For Ni-catalyzed reactions, see: (j) Yamamoto, T.; Morita, T.; Takagi, J.; Yamakawa, T. *Org. Lett.* **2011**, *13*, 5766. (k) Huang, K.; Yu, D.-G.; Zheng, S.-F.; Wu, Z.-H.; Shi, Z.-J. *Chem.—Eur. J.* **2011**, *17*, 786. For Cu-catalyzed reactions, see: (l) Kleeberg, C.; Dang, L.; Lin, Z. Y.; Marder, T. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 5350.

(12) Recently, transition-metal-free borylation using silylborane has been reported, and a reaction mechanism similar to that in Scheme 2 has been proposed (mentioned in SI): (a) Yamamoto, E.; Izumi, K.; Horita, Y.; Ito, H. *J. Am. Chem. Soc.* **2012**, *134*, 19997. For the related Mg-catalyzed borylation of benzyl halides using pinacolborane, see: (b) Pintaric, C.; Olivero, S.; Gimbert, Y.; Chavant, P. Y.; Duñach, E. *J. Am. Chem. Soc.* **2010**, *132*, 11825.

(13) Not only the radical-clock experiment (Table 2, entry 21) but also a radical scavenger experiment with 9,10-dihydroanthracene suggested that a radical mechanism is not involved. In addition, the results of control experiments [without Et₂Zn (Table 1, entry 14), or B₂(pin)₂] supported the proposed mechanism via *in situ* generation of borylzincate (Scheme 1). For details, see SI.

(14) Diborylations of benzynes using Pt or Cu catalyst have been reported: (a) Yoshida, H.; Okada, K.; Kawashima, S.; Tanino, K.; Ohshita, J. *Chem. Commun.* **2010**, *46*, 1763. (b) Yoshida, H.; Kawashima, S.; Takemoto, Y.; Okada, K.; Ohshita, J.; Takaki, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 235.

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(16) The reaction of eq 1 (bottom of Table 3) did not proceed at all in the absence of Et₂Zn (or even with NaO^tBu (1.1 equiv) as an activator for diboron). These results indicate that activation of diboron by Lewis base (F⁻ or ^tBuO⁻) is not sufficient for reaction with benzyne, and the desired product was not formed. Thus, formation of borylzincate species is crucial for this transformation. For details, see SI.

(17) In the case of our previous reported silylzincation of alkynes, the use of magnesium cation was effective. See also ref 4a and SI.

(18) Various methods of Pt- or Cu-catalyzed borylations of alkynes have been reported. For reviews, see ref 5.