Title	Copper-catalyzed direct borylation of alkyl, alkenyl and aryl halides with B(dan)
Author(s)	Yoshida, Hiroto; Takemoto, Yuki; Kamio, Shintaro; Osaka, Itaru; Takaki, Ken
Citation	Organic Chemistry Frontiers , 4 (7) : 1215 - 1219
Issue Date	2017-04-10
DOI	10.1039/C7QO00084G
Self DOI	
URL	https://ir.lib.hiroshima-u.ac.jp/00048764
Right	This journal is © the Partner Organisations 2017 This is not the published version. Please cite only the published version. この論文は出版社版でありません。引用の際には出版社版をご確認、ご利用ください。
Relation	

Journal Name

ARTICLE

Copper-catalyzed direct borylation of alkyl, alkenyl and aryl halides with B(dan)

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Hiroto Yoshida,* Yuki Takemoto, Shintaro Kamio, Itaru Osaka and Ken Takaki

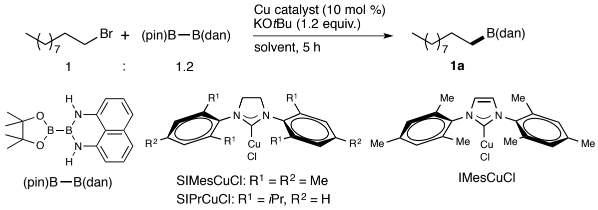
Substitutional borylation of C(sp^3 or sp^2)–halogen bonds with an unsymmetrical diboron [(pin)B–B(dan)] was found to proceed smoothly under copper catalysis. A variety of masked alkyl-, alkenyl- and arylboron compounds [R–B(dan)] were straightforwardly accessible with high functional group compatibility in high yield.

Introduction

Boron-masking-unmasking strategy has assuredly opened up a new vista of modern organoboron chemistry,[1,2] especially in accessing such invaluable molecules as oligoarenes[1a-d,f] and natural products[2a-c,h,k,n] via iterative cross-coupling processes. The representative masked organoboron compounds used for this purpose are R–B(dan) (dan: 1,8-diaminonaphthalene) and R–B(mida) (mida: *N*-methyliminodiacetic acid), being generally prepared by replacement of substituents on preformed organoboronic acids or esters by dan[1a,b,3] or mida,[2] and thus the structural diversity of the available masked organoboron compounds are mainly dependent on those of organoboronic acids and esters that can be synthesized by the existing methods. Because some organoboronic acids/esters are intractable and unstable, development of direct way of installing the masked boryl moieties into organic frameworks[1c-f,4] is of urgent importance in synthetic organic chemistry.

We have recently devoted our attention to developing potential catalysis of a masked borylcopper species [Cu–B(dan)] arising from selective σ-bond metathesis between an unsymmetrical diboron [(pin)B–B(dan)][1e,5] and Cu–OR, and have demonstrated that this borylcopper species has an apparent affinity for unsaturated carbon–carbon bonds, leading to three-component hydroboration[6] and borylstannylation[7] of alkynes and alkenes using an alcohol or a tin alkoxide[8] as an electrophile.[9,10] In view of latent nucleophilicity of the borylcopper species derived from $Cu^{\delta+}$–$B(dan)^{\delta-}$ polarization,[11] we envisaged that electrophilic carbon center of organic halides should exhibit high reactivity toward the masked borylcopper species. We report herein on the copper-catalyzed formal nucleophilic substitution of organic halides with a B(dan) moiety, which provides direct access to diverse masked alkyl, alkenyl and arylboron compounds.[12]

Table 1 Optimization of the reaction conditions[a]



Entry	Cu cat.	Solvent	Temp. (°C)	Yield (%)[b]
1	$(PPh_3)_3CuCl$	THF	50	71
2[c]	CuCl, xantphos	THF	50	57
3	SIPrCuCl	THF	50	69
4	IMesCuCl	THF	50	75
5	SIMesCuCl	THF	50	80
6	SIMesCuCl	Toluene	50	58
7	SIMesCuCl	DMF	50	77
8	none	THF	50	0
9[d]	SIMesCuCl	THF	50	0
10[e]	SIMesCuCl	THF	10	87
11[f]	SIMesCuCl	THF	50	41
12[g]	SIMesCuCl	THF	10	91

[a] Conditions: 1-bromodecane (0.30 mmol), diboron (0.36 mmol), KO*t*Bu (0.36 mmol), Cu catalyst (0.030 mmol), solvent (1 mL), 5 h. [b] Isolated yield. [c] CuCl/xantphos = 1. [d] K_3PO_4 (0.30 mmol) was used instead of KO*t*Bu. [e] SIMesCuCl: 5 mol %, time: 1 h. [f] SIMesCuCl: 1 mol %. [g] SIMesCuCl: 1 mol %, time: 14 h.

Results and discussion

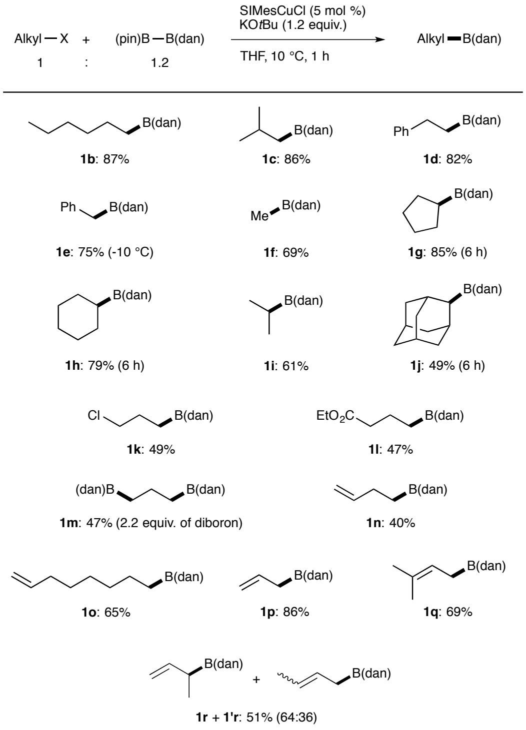
Our effort was initially focused upon the reaction of 1-bromodecane with (pin)B–B(dan) to observe that the C–Br bond was substituted by B(dan) in the presence of KO*t*Bu and $(PPh_3)_3CuCl$ catalyst, giving a 71% yield of **1a** without any formation of the respective pinacol boronate (entry 1, Table 1).[12b-e] Other ligands (xantphos and NHC) and solvents could also be used for this transformation, and a combination of SIMes and THF turned out to be optimum (entries 2–7). No substitution occurred in the absence of the copper catalyst

---

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan. E-mail: yhiroto@hiroshima-u.ac.jp

† Electronic Supplementary Information (ESI) available: Experimental procedures and compound characterization data for all new compounds. See DOI: 10.1039/x0xx00000x

Table 2 Scope of alkyl halides[a]



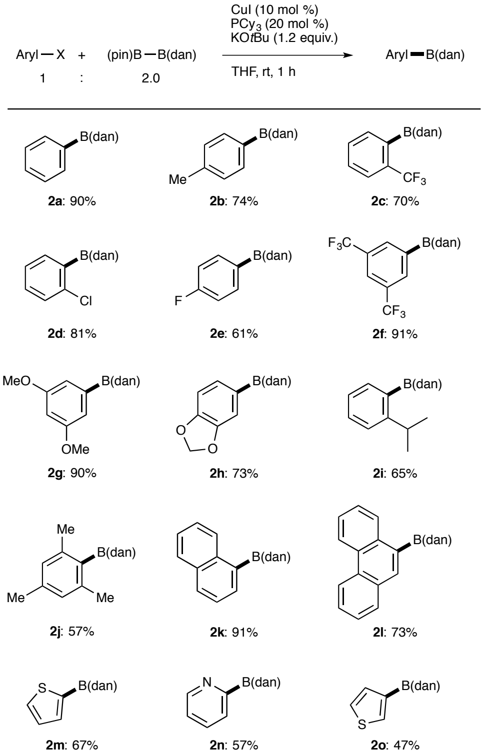
[a] Isolated yield. Conditions: alkyl halide (0.30 mmol), diboron (0.36 mmol), KO*t*Bu (0.36 mmol), SIMesCuCl (0.015 mmol), THF (1 mL), 10 °C, 1 h.

(entry 8), and the use of a weak base (K_3PO_4) also inhibited the reaction (entry 9). By conducting the reaction at 10 °C, the amount of the catalyst was found to be reduced to 5 mol % and 1 mol % without loss of the product yield, although prolonged reaction time was necessary for completion in the latter case (entries 10–12).

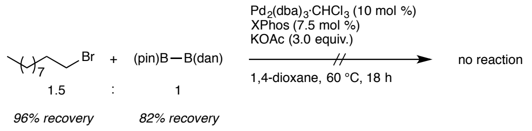
A variety of primary alkyl halides bearing a C–Br or a C–I bond (I for **1b** and **1f**, Br for the others) were facilely convertible into the corresponding masked alkylboron compounds (**1b**–**1f**) under the optimized conditions (Table 2), and the reaction of secondary alkyl bromides (**1g**–**1j**) smoothly proceeded regardless of the steric hindrance, whereas a desired product was not formed at all with *tert*-butyl bromide. A C–Cl bond (**1k**) and an ester moiety (**1l**) were tolerable throughout the reaction, demonstrating the high functional group compatibility; on the other hand, 1,3-dibromopropane (**1m**) underwent dual borylation. A masked borylcopper species [Cu–B(dan)] showed higher affinity toward a C–Br bond of 4-bromo-1-butene (**1n**) and 8-bromo-1-octene (**1o**), where cyclized products arising from intramolecular carboboration of a C–C double bond were not generated.[12*g*,13] Furthermore, simple allyl bromide (**1p**) could also participate in the reaction, and exclusive α-substitution took place with prenyl bromide (**1q**), while the reaction of crotyl bromide (*E*:*Z* = 84:16) afforded a mixture of α- (**1'r**) and γ-products (**1r**).

The versatility of the substitution reaction with the B(dan) moiety was further expanded by application to C(sp^2)–X bonds (Table 3). Thus, treatment of bromobenzene, (pin)B–B(dan) and KO*t*Bu with CuI–PCy_3 as an optimum catalyst[14] furnished Ph–B(dan) (**2a**) in 90% yield. Monosubstituted aryl bromides (or iodide for **2b**) having a methyl, trifluoromethyl (**2c**), chloro (**2d**) or fluoro (**2e**) moiety could efficiently be transformed into masked aryl boron compounds, in which the Ar–Cl (or F) bond remained intact. In addition to disubstituted aryl bromides which also provided good yields of the products (**2f**–**2h**), sterically bulky (**2i** and **2j**), polycyclic (**2k** and **2l**) and heterocylic (**2m**–**2o**) aryl bromides readily underwent the substitution. A palladium-catalyzed coupling reaction of aryl halides with (pin)B–B(dan) was reported previously,[4*e*] however this system has turned out to be inefficacious for an alkyl halide (Scheme 1), demonstrating the wide applicability of the present reaction.

Table 3 Scope of aryl halides[a]

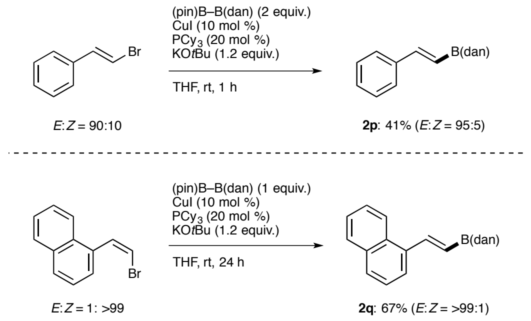


[a] Isolated yield. Conditions: aryl halide (0.30 mmol), diboron (0.60 mmol), KO*t*Bu (0.36 mmol), CuI (0.030 mmol), PCy_3 (0.060 mmol), THF (1 mL), rt, 1 h.

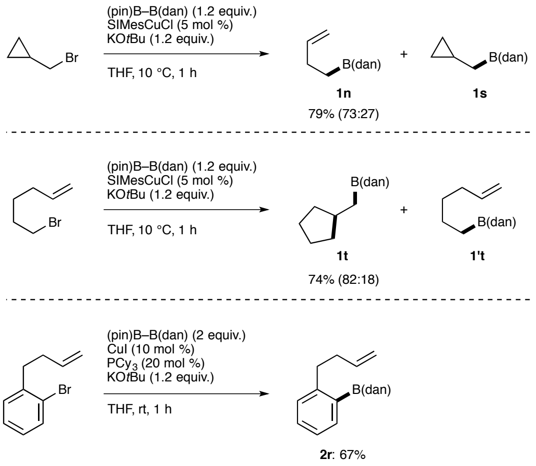


Scheme 1 Pd-catalyzed reaction of 1-bromodecane with (pin)B–B(dan)

The reaction was also found to be applicable to alkenyl bromides (Scheme 2), which would give some insights into the reaction pathway: both (*E*)- and (*Z*)-alkenyl bromides preferentially provided (*E*)-alkenyl boron compounds (**2p** and **2q**), implying the intermediacy of an alkenyl radical in the present substitution, because a parent vinyl radical has been reported to be rapidly interconverting ($k = 4.0 \times 10^{10}$ s^{-1} at 300 K) due to an inversion barrier as low as 3 kcal/mol.[15] The



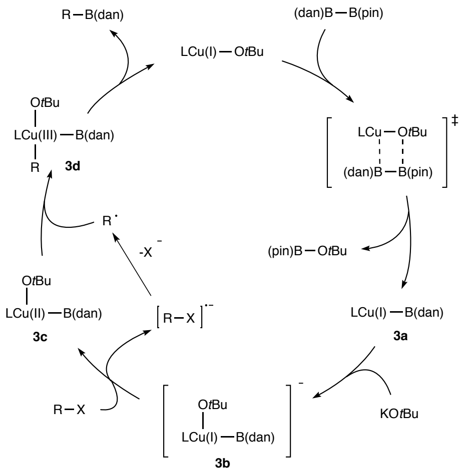
Scheme 2 Stereochemistry with alkenyl bromides



Scheme 3 Radical clock reactions

involvement of a radical intermediate in the C(sp^3)–Br substitution was also strongly supported by the reaction of cyclopropylmethyl bromide[16] or 6-bromo-1-hexene (Scheme 3), leading to the predominant formation of a ring-opened product (**1n**, rate constant for ring opening: $k = 8.6 \times 10^7$ s^{-1} at 298 K)[17] or a cyclized product (**1t**, rate constant for ring closure: $k = 2.3 \times 10^5$ s^{-1} at 298 K).[18,19] In contrast, 2-(3-butenyl)phenyl bromide afforded the simple substitution product (**2r**) in 67% yield, although the respective aryl radical is apt to undergo cyclization (rate constant for ring closure: $k = 5.0 \times 10^8$ s^{-1} at 323 K).[20]

The above results indicate that the present reaction includes one-electron reduction of organic halides as a key step, and thus we propose a catalytic cycle, which commences with the formation of a masked borylcopper species [Cu–B(dan)] (**3a**) via selective interaction between Lewis acidic B(pin) and Lewis basic O*t*Bu in σ-bond metathesis step (Scheme 4).[6,7,9] Then KO*t*Bu coordinates to **3a** to generate an electron-rich borylcuprate species (**3b**), which may serve as a one-electron reductant for an organic halide.[12g,21] Subsequent elimination of X$^-$ from the resulting radical anion which generates an isomerizable free radical (*cf.* Schemes 2 and 3), followed by combination of the radical with [*t*BuO–Cu(II)–B(dan)] (**3c**) gives a Cu(III) complex (**3d**).[22] Finally, **3d** undergoes reductive elimination to afford a masked organoboron compounds with regeneration of Cu–O*t*Bu.[23,24] The exceptional result with 2-(3-butenyl)phenyl bromide may be construed that an aryl radical was instantaneously captured by **3c** before ring closure or that a isomerization-resistant radical anion[25] directly reacted with **3c**.



Scheme 4 Proposed catalytic cycle

Conclusions

In conclusion, we have developed the direct and potent method for installing a B(dan) moiety into organic frameworks through the copper-catalyzed substitution of C(sp^3 or sp^2)–X bonds which gives diverse masked alkyl-, alkenyl- and arylboron compounds of high synthetic utility, and have demonstrated that the reaction includes one-electron transfer process, being in marked contrast to the cases of the previous copper-catalyzed B(dan)-installing reactions into unsaturated C–C bonds.[6,7] Further studies on the catalytic utilization of the Cu–B(dan) species for the direct synthesis of masked organoboron compounds as well as on the details of the mechanism are in progress.

Acknowledgements

This paper is dedicated to Prof. Tamejiro Hiyama (Chuo University, Japan) on the occasion of his 70th birthday. The authors acknowledge helpful discussion on the catalytic cycle with Prof. Eiji Shirakawa (Kwansei Gakuin University, Japan). This work was financially supported by JSPS KAKENHI Grant Number JP16H01031 in Precisely Designed Catalysts with Customized Scaffolding.

Notes and references

1 (*a*) H. Noguchi, K. Hojo and M. Suginome, *J. Am. Chem. Soc.*, 2007, **129**, 758; (*b*) H. Noguchi, T. Shioda, C.-M. Chou and M. Suginome, *Org. Lett.*, 2008, **10**, 377; (*c*) N. Iwadate and M. Suginome, *J. Organomet. Chem.*, 2009, **694**, 1713; (*d*) N. Iwadate and M. Suginome, *Org. Lett.*, 2009, **11**, 1899; (*e*) N. Iwadate and M. Suginome, *J. Am. Chem. Soc.*, 2010, **132**, 2548; (*f*) N. Iwadate and M. Suginome, *Chem. Lett.*, 2010, **39**, 558.

2 (*a*) E. P. Gillis and M. D. Burke, *J. Am. Chem. Soc.*, 2007, **129**, 6716; (*b*) S. J. Lee, K. C. Gray, J. S. Paek and M. D. Burke, *J. Am. Chem. Soc.*, 2008, **130**, 466; (*c*) E. P. Gillis and M. D. Burke, *J. Am. Chem. Soc.*, 2008, **130**, 14084; (*d*) B. E. Uno, E. P Gillis and M. D. Burke, *Tetrahedron*, 2009, **65**, 3130; (*e*) D. M. Knapp, E. P. Gillis and M. D. Burke, *J. Am. Chem. Soc.*, 2009, **131**, 6961; (*f*) J. R. Struble, S. J. Lee and M. D. Burke, *Tetrahedron*, 2010, **66**, 4710; (*g*) G. R. Dick, D. M. Knapp, E. P Gillis and M. D. Burke, *Org. Lett.*, 2010, **12**, 2314; (*h*) E. M. Woerly, A. H. Cherney, E. K. Davis and M. D. Burke, *J. Am. Chem. Soc.*, 2010, **132**, 6941; (*i*) S. J. Lee, T. M. Anderson and M. D. Burke, *Angew. Chem. Int. Ed.*, 2010, **49**, 8860; (*j*) E. M. Woerly, J. R. Struble, N. Palyam, S. P. O'Hara and M. D. Burke, *Tetrahedron*, 2011, **67**, 4333; (*k*) S. Fujii, S. Y. Chang and M. D. Burke, *Angew. Chem. Int. Ed.*, 2011, **50**, 7862; (*l*) G. R. Dick, E. M. Woerly and M. D. Burke, *Angew. Chem. Int. Ed.*, 2012, **51**, 2667; (*m*) E. M. Woerly, J. E. Miller and M. D. Burke, *Tetrahedron*, 2013, **69**, 7732; (*n*) E. M. Woerly, J. Roy and M. D. Burke, *Nat. Chem.*, 2014, **6**, 484.

3 G. Kaupp, R. Naimi-Jamal and V. Stepanenko, *Chem. Eur. J.*, 2003, **9**, 4156.

4 (*a*) J. Cid, J. J. Carbó and E. Fernández, *Chem. Eur. J.*, 2014, **20**, 3616; (*b*) Y. Nagashima, K. Hirano, R. Takita and M. Uchiyama, *J. Am. Chem. Soc.*, 2014, **136**, 8532; (*c*) T. Tsuchimoto, H. Utsugi, T. Sugiura and S. Horio, *Adv. Synth. Catal.*, 2015, **357**, 77; (*d*) N. Miralles, J. Cid, A. B. Cuenca, J. J. Carbó and E. Fernández, *Chem. Commun.*, 2015, **51**, 1693; (*e*) L. Xu and P. Li, *Chem. Commun.*, 2015, **51**, 5656; (*f*) X. Guo, A. K. Nelson, C. Slebodnick and W. L. Santos, *ACS Catal.*, 2015, **5**, 2172; (*g*) N. Miralles, R. M. Romero, E. Fernández and K. Muñiz, *Chem. Commun.*, 2015, **51**, 14068; (*h*) A. B. Cuenca, J. Cid, D. García-López, J. J. Carbó and E. Fernández, *Org. Biomol. Chem.*, 2015, **13**, 9659; (*i*) W. J. Jang, W. L. Lee, J. H. Moon, J. Y. Lee and J. Yun, *Org. Lett.*, 2016, **18**, 1390; (*j*) K. Chen, S. Zhang, P. He and P. Li, *Chem. Sci.*, 2016, **7**, 3676; (*k*) Z. Majzik, A. B. Cuenca, N. Pavliček, N. Miralles, G. Meyer, L. Gross and E. Fernández, *ACS Nano*, 2016, **10**, 5340.

5 The diboron was readily prepared from diaminonaphthalene and bis(pinacolato)diboron. See: ref. 6*a*.

6 (*a*) H. Yoshida, Y. Takemoto and K. Takaki, *Chem. Commun.*, 2014, **50**, 8299; (*b*) H. Yoshida, Y. Takemoto and K. Takaki, *Asian J. Org. Chem.*, 2014, **3**, 1204.

7 H. Yoshida, Y. Takemoto and K. Takaki, *Chem. Commun.*, 2015, **51**, 6297.

8 We have also reported the copper-catalyzed three-component borylstannylation using bis(pinacolato)diboron as a boron source. See: (*a*) Y. Takemoto, H. Yoshida and K. Takaki, *Chem. Eur. J.*, 2012, **18**, 14841; (*b*) Y. Takemoto, H. Yoshida and K. Takaki, *Synthesis*, 2014, **46**, 3024.

9 For other examples on the copper-catalyzed borylations using (pin)B–B(dan), see: (*a*) R. Sakae, K. Hirano, T. Satoh and M. Miura, *Angew. Chem. Int. Ed.*, 2015, **54**, 613; (*b*) R. Sakae, K. Hirano, T. Satoh and M. Miura, *J. Am. Chem. Soc.*, 2015, **137**, 6460; (*c*) A. K. Nelson, C. L. Peck, S. M. Rafferty and W. L. Santos, *J. Org. Chem.*, 2016, **81**, 4269; (*d*) H. Lee, J. T. Han and J. Yun, *ACS Catal.*, 2016, **6**, 6487; (*e*) D. Nishikawa, K. Hirano and M. Miura, *Org. Lett.*, 2016, **18**, 4856.

10 For our reports on the copper-catalyzed metallation reactions for synthesizing main group organometallics containing boron, tin or silicon, see: (*a*) H. Yoshida, S. Kawashima, Y. Takemoto, K. Okada, J. Ohshita and K. Takaki, *Angew. Chem. Int. Ed.*, 2012, **51**, 235; (*b*) H. Yoshida, I. Kageyuki and K. Takaki, *Org. Lett.*, 2013, **15**, 952; (*c*) H. Yoshida, A. Shinke and K. Takaki, *Chem. Commun.*, 2013, **49**, 11671; (*d*) I. Kageyuki, H. Yoshida and K. Takaki, *Synthesis*, 2014, **46**, 1924; (*e*) H. Yoshida, Y. Hayashi, Y. Ito and K. Takaki, *Chem. Commun.*, 2015, **51**, 9440; (*f*) H. Yoshida, A. Shinke, Y. Kawano and K. Takaki, *Chem. Commun.*, 2015, **51**, 10616; (*g*) H. Yoshida, *Chem. Rec.*, 2016, **16**, 419; (*h*) H. Yoshida, *ACS Catal.*, 2016, **6**, 1799; (*i*) H. Yoshida, *Synthesis*, 2016, **48**, 2540.

11 For pioneering works on the use of a borylcopper species as a boron nucleophile, see: (*a*) K. Takahashi, T. Ishiyama and N. Miyaura, *Chem. Lett.*, 2000, 982; (*b*) H. Ito, H. Yamanaka, J.-I. Tateiwa and A. Hosomi, *Tetrahedron Lett.*, 2000, **41**, 6821; (*c*) K. Takahashi, T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2001, **625**, 47.

12 For the copper-catalyzed formal nucleophilic substitution of organic halides with bis(pinacolato)diboron, see: (*a*) C. Kleeberg, L. Dang, Z. Lin, and T. B. Marder, *Angew. Chem. Int. Ed.*, 2009, **48**, 5350; (*b*) C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czyzewska, P. G. Steel, T. B. Marder and L. Liu, *Angew. Chem. Int. Ed.*, 2012, **51**, 528; (*c*) H. Ito and K. Kubota, *Org. Lett.*, 2012, **14**, 890; (*d*) J. H. Kim and Y. K. Chung, *RSC Adv.*, 2014, **4**, 39755; (*e*) X.-F. Zhou, Y.-D. Wu, J.-J. Dai, Y.-J. Li, Y. Huang and H.-J. Xu, *RSC Adv.*, 2015, **5**, 46672; (*f*) H. Iwamoto, K. Kubota and H. Ito, *Chem. Commun.*, 2015, **51**, 9655; (*g*) K. Kubota, H. Iwamoto, H. Ito, *Org. Biomol. Chem.*, 2017, **15**, 285.

13 For the copper-catalyzed intramolecular carboboration of carbon–carbon double bonds with bis(pinacolato)diboron, see: (*a*) H. Ito, Y. Kosaka, K. Nonoyama, Y. Sasaki and M. Sawamura, *Angew. Chem. Int. Ed.*, 2008, **47**, 7424; (*b*) H. Ito, T. Toyoda and M. Sawamura, *J. Am. Chem. Soc.*, 2010, **132**, 5990; (*c*) C. Zhong, S. Kunii, Y. Kosaka, M. Sawamura and H. Ito, *J. Am. Chem. Soc.*, 2010, **132**, 11440; (*d*) K. Kubota, E. Yamamoto and H. Ito, *J. Am. Chem. Soc.*, 2013, **135**, 2635.

14 For optimization of reaction conditions, see ESI for details.

15 (*a*) C. Galli, A. Guarnieri, H. Koch, P. Mencarelli and Z. Rappoport, *J. Org. Chem.*, 1997, **62**, 4072; (*b*) T. P. M. Goumans, K. van Alem and G. Lodder, *Eur. J. Org. Chem.*, 2008, 435.

16 The copper-catalyzed intermolecular carboboration using bis(pinacolato)diboron and cyclopropylmethyl bromide proceeded without ring-opening, being in marked contrast to the result described herein. See: refs. 10*b* and *d*.

17 V. W. Bowry, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.*, 1991, **113**, 5687.

18 (*a*) C. Chatgilialoglu, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1981, **103**, 7739; (*b*) Y. Fu, R.-Q. Li, L. Liu and Q.-X. Guo, *Res. Chem. Intermediat.*, 2004, **30**, 279.

19 The involvement of a radical intermediate was also reported in the copper-catalyzed substitution of alkyl halides with bis(pinacolato)diboron. See: refs. 12*b*–*d*.

20 A. N. Abeywickrema and A. L. J. Beckwith, *J. Chem. Soc., Chem. Commun.*, 1986, 464.

21 Potassium *tert*-butoxide has been reported to serve as a one-electron reductant for organic halides, however it generally requires a donating ligand such as 1,10-phenanthroline and/or elevated temperatures, which is in sharp contrast to the conditions employed in the present reaction. For examples, see: (*a*) S. Yanagisawa, K. Ueda, T. Taniguchi and K. Itami, *Org. Lett.*, 2008, **10**, 4673; (*b*) E. Shirakawa, K.-I. Itoh, T. Higashino and T. Hayashi, *J. Am. Chem. Soc.*, 2010, **132**, 15537; (*c*) C.-L. Sun, H. Li, D.-G. Yu, M. Yu, X. Zhou, X.-Y. Lu, K. Huang, S.-F. Zheng, B.-J. Li and Z.-J. Shi, *Nat. Chem.*, 2010, **2**, 1044; (*d*) E. Shirakawa, X. Zhang and T. Hayashi, *Angew. Chem. Int. Ed.*, 2011, **50**, 4671.

22 For a review on high-valent copper [Cu(III)] species, see: A. J. Hickman and M. S. Sanford, *Nature*, 2012, **484**, 177.

23 For borylation reactions of organic halides under other transition metal catalysis which include the formation of a radical intermediate, see: (*a*) J. Yi, J.-H. Liu, J. Liang, J.-J. Dai, C.-T. Yang, Y. Fu and L. Liu, *Adv. Synth. Catal.*, 2012, **354**, 1685; (*b*) A. S. Dubnik and G. C. Fu, *J. Am. Chem. Soc.*, 2012, **134**, 10693; (*c*) S. K. Bose, K. Fucke, L. Liu, P. G. Steel and T. B. Marder, *Angew. Chem. Int. Ed.*, 2014, **53**, 1799; (*d*) S. K. Bose,

A. Deibenberger, A. Eichhorn, P. G. Steel, Z. Lin and T. B. Marder, *Angew. Chem. Int. Ed.*, 2015, **54**, 11843; (*e*) T. C. Atack and S. P. Cook, *J. Am. Chem. Soc.*, 2016, **138**, 6139.

24 An alternative pathway involving σ-bond metathesis between Cu–B(dan) and organic halides may also be possible. See: ref. 12*a*.

25 N. Uchiyama, E. Shirakawa and T. Hayashi, *Chem. Commun.*, 2013, **49**, 364.