Platinum-catalysed diborylation of arynes: synthesis and reaction of 1,2-diborylarenes†

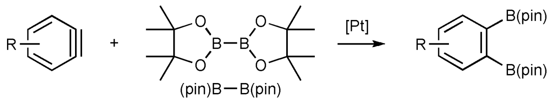
Hiroto Yoshida,* Kengo Okada, Shota Kawashima, Kenji Tanino and Joji Ohshita

Received (in Cambridge, UK) 17th September 2009, Accepted 25th November 2009
First published as an Advance Article on the web 13th January 2010
DOI: 10.1039/b919407j

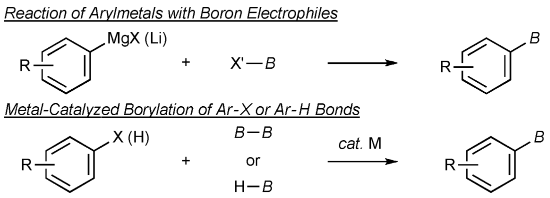
Arynes are found to be facilely inserted into bis(pinacolato)-diboron by using a platinum–isocyanide catalyst, affording diverse 1,2-diborylarenes, which can be converted into *o*-terphenyls *via* Suzuki–Miyaura coupling reaction.

Arylboron compounds are invaluable reagents in synthetic organic chemistry[1] for constructing diverse functional molecules *via* Suzuki–Miyaura coupling,[2] Petasis reaction,[3] *etc*. While a variety of arylboron compounds can be prepared by a reaction of aryl Grignard reagents (or aryllithiums) with boron electrophiles and transition metal-catalysed borylation of Ar–X (X = halogen or OTf)[4] or Ar–H bonds (Scheme 1),[5] the development of new synthetic approaches is still of great importance.[6]

We have already disclosed that the strained carbon–carbon triple bond of arynes could smoothly be inserted into metal-containing σ-bonds (C–Sn,[7] Sn–Sn[8] or Si–Si[9]) in the presence of a palladium catalyst, giving various arylstannanes and arylsilanes in a straightforward manner. In view of the controllable properties of arynes toward the insertion reaction with the aid of transition metal catalysis,[10] we envisaged that a new method for synthesizing arylboron compounds would be feasible depending upon the catalytic insertion reaction of arynes into a boron-containing σ-bond.[11] We report herein that a platinum–isocyanide complex efficaciously catalyses an insertion reaction of arynes into the B–B bond of bis(pinacolato)-diboron [(pin)B–B(pin)] to produce 1,2-diborylarenes, which are difficult to access using conventional methods (eqn (1)).[12]

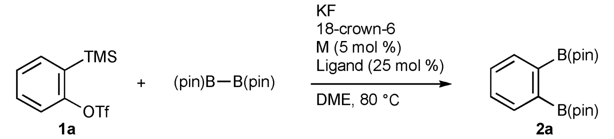


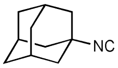
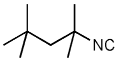
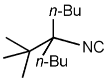
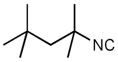
(1)



Scheme 1 Representative methods for preparing arylboron compounds.

Table 1 Catalyst screening for diborylation[a]



Entry	M	Ligand	Time/h	Yield (%)[b]
1	$Pt(dba)_2$		23	77
2	$Pt(dba)_2$		48	76
3	$Pt(dba)_2$		22	61
4	$Pt(dba)_2$	CyNC	22	10
5	$Pt(dba)_2$	Ph_3CNC	99	10
6	$Pt(dba)_2$	None	16	0
7	$Pt(PPh_3)_4$	None	16	0
8	$Pd(OAc)_2$		23	0

[a] The reaction was carried out in DME at 80 °C using **1a** (0.060 mmol), (pin)B–B(pin) (0.084 mmol), KF (0.12 mmol), 18-crown-6 (0.12 mmol), M (3.0 μmol) and ligand (0.015 mmol). [b] Isolated yield based on **1a**.

The diborylation was found to facilely proceed in DME at 80 °C when *in situ*-generated benzyne (from **1a**[13] and KF/18-crown-6) was treated with (pin)B–B(pin) in the presence of $Pt(dba)_2$ and 1-adamantyl isocyanide (1-AdNC), giving 1,2-diborylbenzene (**2a**) in 77% yield (Table 1, entry 1). Isocyanides bearing another *tert*-alkyl substituent also promoted the diborylation (entries 2 and 3), whereas the reaction using cyclohexyl or trityl isocyanide became sluggish (entries 4 and 5). The combination of $Pt(dba)_2$ and an isocyanide ligand has proven to be vital for the diborylation, and thus, other platinum complexes ($Pt(PPh_3)_4$ or $Pt(dba)_2$: a catalyst for diborylation of alkynes[14] or alkenes[15]) and a palladium–isocyanide complex (a catalyst for disilylation[9] and distannylation[8] of arynes) did not afford the desired product at all (entries 6–8).[16]

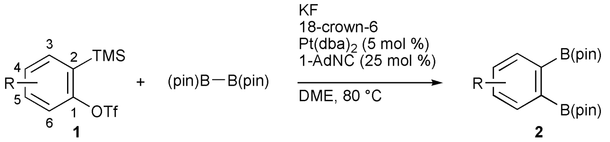
By using the optimized catalyst ($Pt(dba)_2$–1-AdNC), 4-substituted arynes (from **1b–1e**) and 3-methylbenzyne (from **1f**) could also participate in the diborylation to provide the respective diborylarenes (**2b–2f**) in high yields (Table 2, entries 1–5). The use of disubstituted arynes further elevated the versatility of the reaction. Thus, 3,4-dimethoxy- and 4,5-dimethyl-1,2-diborylbenzene (**2g** and **2h**) were readily available from the corresponding arynes in 67% and 80% yield (entries 6 and 7), and moreover, 3,6-dimethoxybenzyne

---

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan. E-mail: yhiroto@hiroshima-u.ac.jp; Fax: +81-82-424-5494; Tel: +81-82-424-7724

† Electronic supplementary information (ESI) available: Experimental procedures including spectroscopic and analytical data. See DOI: 10.1039/b919407j

Table 2 Platinum-catalysed diborylation of arynes[a]



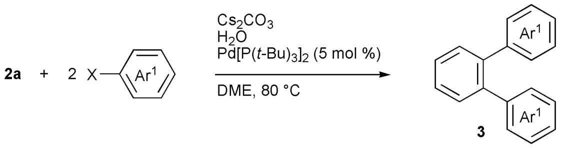
Entry	R	Time/h	Yield (%)[b]	2
1	4-MeO (**1b**)	43	78	**2b**
2	4-Me (**1c**)	49	73	**2c**
3	4-F (**1d**)	16	73	**2d**
4	4-Ph (**1e**)	14	67	**2e**
5	6-Me (**1f**)	30	84	**2f**
6	3,4-(MeO)$_2$ (**1g**)	47	67	**2g**
7[c]	4,5-Me$_2$ (**1h**)	21	80	**2h**
8	3,6-(MeO)$_2$ (**1i**)	45	50	**2i**
9	3,6-Me$_2$ (**1j**)	41	44	**2j**

[a] The reaction was carried out in DME at 80 °C using **1** (0.060 mmol), (pin)B–B(pin) (0.084 mmol), KF (0.12 mmol), 18-crown-6 (0.12 mmol), Pt(dba)$_2$ (3.0 mol) and 1-AdNC (0.015 mmol). [b] Isolated yield based on **1**. [c] KF = 0.24 mmol, 18-crown-6 = 0.24 mmol.

(from **1i**) and 3,6-dimethylbenzyne (from **1j**) underwent the diborylation as well, despite steric congestion around the triple bond (entries 8 and 9).

We next examined Suzuki–Miyaura coupling of the resulting diborylarenes with aryl halides in order to demonstrate their synthetic utility, and found that variously substituted *ortho*-terphenyls could be prepared in a straightforward manner.[17,18] As depicted in Table 3, treatment of **2a** with iodobenzene (2.2 eq.) using Pd[P(t-Bu)$_3$]$_2$ as catalyst and Cs$_2$CO$_3$ furnished the doubly coupled product **3a** in 85% yield (entry 1). Aryl iodides bearing Ac, NO$_2$, CN, Me or OMe at the *para* position were smoothly coupled with **2a** regardless of their electronic properties, giving symmetrical *ortho*-terphenyls **3b–3f** in good yields (entries 2–6), and 3-thienyl and 1-naphthyl moieties could also be introduced *via* the coupling (entries 7 and 8). Under similar reaction conditions, a 1 : 1 coupling reaction of **2a** with 1,8-dihalonaphthalenes proceeded efficiently to provide fluoranthene derivatives (**3i** and **3j**) in one step (Scheme 2).[19,20]

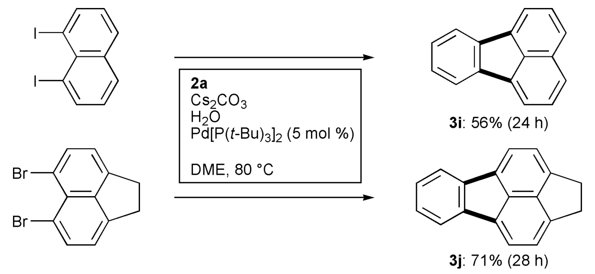
Table 3 Synthesis of symmetrical *ortho*-terphenyls *via* Suzuki–Miyaura coupling[a]



Entry	Ar^1–X	Time/h	Yield (%)[b]	3
1	Ph–I	29	85	**3a**
2	4-AcC$_6$H$_4$–I	36	82	**3b**
3	4-O$_2$NC$_6$H$_4$–I	46	72	**3c**
4	4-NCC$_6$H$_4$–I	74	64	**3d**
5	4-MeC$_6$H$_4$–I	52	64	**3e**
6	4-MeOC$_6$H$_4$–I	39	55	**3f**
7	3-Thienyl–Br	19	74	**3g**
8	1-Naphthyl–I	39	74	**3h**

[a] The reaction was carried out in DME at 80 °C using **2a** (0.039 mmol), an aryl halide (0.086 mmol), Cs$_2$CO$_3$ (0.090 mmol), H$_2$O (15 μL) and Pd[P(t-Bu)$_3$]$_2$ (2.0 μmol). [b] Isolated yield based on **2a**.

Furthermore, the coupling reaction using diborylarene **2a** was extended to the synthesis of unsymmetrical *ortho*-terphenyls (Table 4). At first, **2a** was transformed into the monoborylbiphenyl by reaction with iodobenzene (1.0 eq.) in the presence of Pd(PPh$_3$)$_4$ catalyst and KOH. Subsequent coupling reaction with electron-deficient (entries 1–3) or -rich (entries 4–6) aryl halides took place successfully to afford **4a–4f**, and in addition, 1-naphthyl, 9-phenanthryl and 9-anthryl halides of steric hindrance also underwent coupling with high efficiencies (entries 7–9).[21]

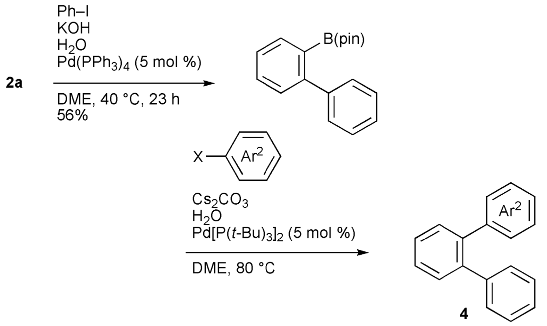


Scheme 2 Synthesis of fluoranthene derivatives *via* Suzuki–Miyaura coupling.

Successive addition of aryl halides allowed the entire coupling process to be performed in one batch, where unsymmetrical *ortho*-terphenyl **4j** was obtainable in 43% yield without isolation of the intermediary monoborylbiaryl (Scheme 3). Various monoborylbiaryls (**5a–5c**) could also be synthesized by a 1 : 1 coupling reaction of **2a** with aryl iodides (Scheme 4).

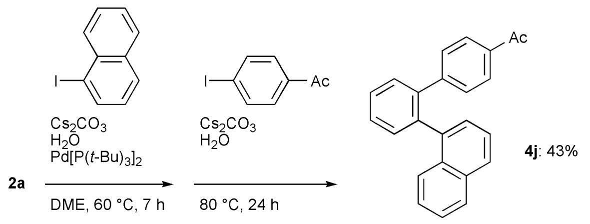
In conclusion, we have demonstrated that the diborylation of arynes smoothly proceeded by employing a platinum–isocyanide catalyst, and that the Suzuki–Miyaura coupling reaction of the resulting 1,2-diborylarenes gave a convenient approach for the synthesis of *ortho*-terphenyls of structural

Table 4 Synthesis of unsymmetrical *ortho*-terphenyls *via* stepwise Suzuki–Miyaura coupling[a]

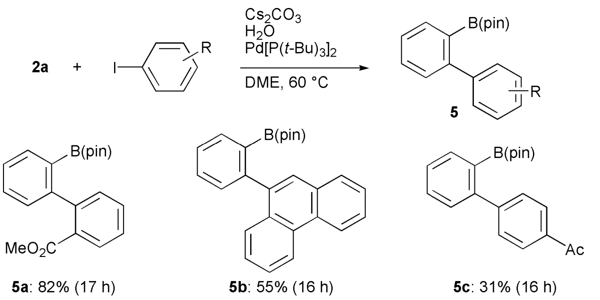


Entry	Ar^2–X	Time/h	Yield (%)[b]	4
1	4-AcC$_6$H$_4$–I	22	93	**4a**
2	4-O$_2$NC$_6$H$_4$–I	16	86	**4b**
3	4-NCC$_6$H$_4$–I	18	72	**4c**
4	4-MeC$_6$H$_4$–I	21	85	**4d**
5	4-MeOC$_6$H$_4$–I	21	68	**4e**
6	3-Thienyl–Br	29	87	**4f**
7	1-Naphthyl–I	19	87	**4g**
8	9-Phenanthryl–I	24	81	**4h**
9	9-Anthryl–Br	4	64	**4i**

[a] The reaction was carried out in DME at 80 °C using monoborylbiphenyl (0.039 mmol), an aryl halide (0.043 mmol), Cs$_2$CO$_3$ (0.045 mmol), H$_2$O (7.5 μL) and Pd[P(t-Bu)$_3$]$_2$ (2.0 μmol). [b] Isolated yield based on monoborylbiphenyl.



Scheme 3 One-batch Suzuki–Miyaura coupling of **2a**.



Scheme 4 Synthesis of borylbiaryls *via* Suzuki–Miyaura coupling.

diversity, which attract considerable attention due to their pharmacological activity.[22] Further studies on the catalytic cycle of the diborylation as well as on a catalytic insertion reaction of arynes into other σ-bonds are in progress.

This work was financially supported by Kinki Invention Center and Electric Technology Research Foundation of Chugoku. We thank Central Glass Co. Ltd. for a generous gift of trifluoromethanesulfonic anhydride.

Notes and references

1 (*a*) A. Pelter, K. Smith and H. C. Brown, *Borane Reagents*, Academic Press, London, 1988; (*b*) *Boronic Acids*, ed. D. G. Hall, Wiley-VCH, Weinheim, 2005.

2 (*a*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (*b*) N. Miyaura, *Top. Curr. Chem.*, 2002, **219**, 11.

3 (*a*) N. A. Petasis, A. Goodman and I. A. Zavialov, *Tetrahedron*, 1997, **53**, 16463; (*b*) T. Koolmeister, M. Södergren and M. Scobie, *Tetrahedron Lett.*, 2002, **43**, 5965.

4 (*a*) T. Ishiyama, M. Murata and N. Miyaura, *J. Org. Chem.*, 1995, **60**, 7508; (*b*) M. Murata, T. Oyama, S. Watanabe and Y. Masuda, *J. Org. Chem.*, 2000, **65**, 164; (*c*) T. Ishiyama, K. Ishida and N. Miyaura, *Tetrahedron Lett.*, 2001, **57**, 9813; (*d*) A. Fürstner and G. Seidel, *Org. Lett.*, 2002, **4**, 541; (*e*) C. Kleeberg, L. Dang, Z. Lin and T. B. Marder, *Angew. Chem., Int. Ed.*, 2009, **48**, 5350.

5 (*a*) H. Chen and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 1999, **38**, 3391; (*b*) C. N. Iverson and M. R. Smith, III, *J. Am. Chem. Soc.*, 1999, **121**, 7696; (*c*) J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka, Jr. and M. R. Smith, III, *Science*, 2002, **295**, 305; (*d*) T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi and J. F. Hartwig, *J. Am. Chem. Soc.*, 2002, **124**, 390; (*e*) T. Ishiyama, Y. Nobuta, J. F. Hartwig and N. Miyaura, *Chem. Commun.*, 2003, 2924.

6 (*a*) M. W. Davies, C. N. Johnson and J. P. A. Harrity, *Chem. Commun.*, 1999, 2107; (*b*) Y. Yamamoto, K. Hattori, J. Ishii and H. Nishiyama, *Tetrahedron*, 2006, **62**, 4294; (*c*) P. M. Delaney, D. L. Browne, H. Adams, A. Plant and J. P. A. Harrity, *Tetrahedron*, 2008, **64**, 866.

7 H. Yoshida, Y. Honda, E. Shirakawa and T. Hiyama, *Chem. Commun.*, 2001, 1880.

8 (*a*) H. Yoshida, K. Tanino, J. Ohshita and A. Kunai, *Angew. Chem., Int. Ed.*, 2004, **43**, 5052; (*b*) H. Yoshida, K. Tanino, J. Ohshita and A. Kunai, *Chem. Commun.*, 2005, 5678.

9 (*a*) H. Yoshida, J. Ikadai, M. Shudo, J. Ohshita and A. Kunai, *J. Am. Chem. Soc.*, 2003, **125**, 6638; (*b*) H. Yoshida, J. Ikadai, M. Shudo, J. Ohshita and A. Kunai, *Organometallics*, 2005, **24**, 156; (*c*) J. Ikadai, H. Yoshida, J. Ohshita and A. Kunai, *Chem. Lett.*, 2005, **34**, 56.

10 For recent examples of transition metal-catalysed reactions of arynes, see: (*a*) M. Jeganmohan, S. Bhuvaneswari and C.-H. Cheng, *Angew. Chem., Int. Ed.*, 2009, **48**, 391; (*b*) H. Yoshida, T. Morishita, H. Nakata and J. Ohshita, *Org. Lett.*, 2009, **11**, 373; (*c*) T. Gerfaud, L. Neuville and J. Zhu, *Angew. Chem., Int. Ed.*, 2009, **48**, 572; (*d*) S. A. Worlikar and R. C. Larock, *Org. Lett.*, 2009, **11**, 2413; (*e*) S.-F. Pi, B.-X. Tang, J.-H. Li, Y.-L. Liu and Y. Liang, *Org. Lett.*, 2009, **11**, 2309; (*f*) Z. Qiu and Z. Xie, *Angew. Chem., Int. Ed.*, 2009, **48**, 5729.

11 For reviews on catalytic insertion reactions of unsaturated carbon–carbon bonds into an element–element σ-bond, see: (*a*) T. B. Marder and N. C. Norman, *Top. Catal.*, 1998, **5**, 63; (*b*) I. Beletskaya and C. Moberg, *Chem. Rev.*, 1999, **99**, 3435; (*c*) M. Suginome and Y. Ito, *Chem. Rev.*, 2000, **100**, 3221; (*d*) I. Beletskaya and C. Moberg, *Chem. Rev.*, 2006, **106**, 2320.

12 Few reports are available on the selective synthesis of 1,2-bis(pinacolatoboryl)arenes: (*a*) M. Shimizu, K. Shimono, T. Kurahashi, S. Kiyomoto, I. Nagao and T. Hiyama, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 518; (*b*) M. Shimizu, I. Nagao, Y. Tomioka and T. Hiyama, *Angew. Chem., Int. Ed.*, 2008, **47**, 8096. For synthesis of other 1,2-diborylarenes, see; (*c*) K. Nozaki, M. Yoshida and H. Takaya, *Angew. Chem., Int. Ed. Engl.*, 1995, **33**, 2452; (*d*) K. Nozaki, M. Yoshida and H. Takaya, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2043; (*e*) H. Noguchi, T. Shioda, C.-M. Chou and M. Suginome, *Org. Lett.*, 2008, **10**, 377.

13 Y. Himeshima, T. Sonoda and H. Kobayashi, *Chem. Lett.*, 1983, 1211.

14 (*a*) T. Ishiyama, N. Matsuda, N. Miyaura and A. Suzuki, *J. Am. Chem. Soc.*, 1993, **115**, 11018; (*b*) T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki and N. Miyaura, *Organometallics*, 1996, **15**, 713; (*c*) G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg and N. C. Norman, *Organometallics*, 1996, **15**, 5137; (*d*) C. N. Iverson and M. R. Smith, III, *Organometallics*, 1996, **15**, 5155; (*e*) R. Ll. Thomas, F. E. S. Souza and T. B. Marder, *J. Chem. Soc., Dalton Trans.*, 2001, 1650.

15 T. Ishiyama, M. Yamamoto and N. Miyaura, *Chem. Commun.*, 1997, 689.

16 Control experiments with substrates in the presence of 1-AdNC or with substrates only did not give **2a** at all.

17 Suzuki–Miyaura coupling of diborylalkenes, see: (*a*) S. D. Brown and R. W. Armstrong, *J. Am. Chem. Soc.*, 1996, **118**, 6331; (*b*) M. Shimizu, C. Nakamaki, K. Shimono, M. Schelper, T. Kurahashi and T. Hiyama, *J. Am. Chem. Soc.*, 2005, **127**, 12506; (*c*) H. Prokopcová, J. Ramírez, E. Fernández and C. O. Kappe, *Tetrahedron Lett.*, 2008, **49**, 4831.

18 For recent reports on catalysed C–H borylation/Suzuki–Miyaura coupling sequences, see: (*a*) P. Harrisson, J. Morris, P. G. Steel and T. B. Marder, *Synlett.*, 2009, 147; (*b*) P. Harrisson, J. Morris, T. B. Marder and P. G. Steel, *Org. Lett.*, 2009, **11**, 3586.

19 The Suzuki–Miyaura coupling of *vic*-diborylphenanthrenes or *vic*-diborylalkenes with 2,2′-dibromobiaryls has recently been disclosed, see ref. 12*b*.

20 For a palladium-catalysed reaction of arynes that gives benzo-annulated structures, see: Z. Liu, X. Zhang and R. C. Larock, *J. Am. Chem. Soc.*, 2005, **127**, 15716.

21 For Suzuki–Miyaura coupling of 2-borylbiaryls, see: (*a*) B. Schilling and D. E. Kaufmann, *Eur. J. Org. Chem.*, 1998, 701; (*b*) P. M. Delaney, J. E. Moore and J. P. A. Harrity, *Chem. Commun.*, 2006, 3323.

22 (*a*) P. Chavatte, S. Yous, C. Marot, N. Baurin and D. Lesieur, *J. Med. Chem.*, 2001, **44**, 3223; (*b*) S. Chakraborty, C. Sengupta and K. Roy, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 4665.