ORGANIC LETTERS

2013
Vol. 15, No. 17
4308–4311

Tetrabutylammonium 2-Pyridyltriolborate Salts for Suzuki–Miyaura Cross-Coupling Reactions with Aryl Chlorides

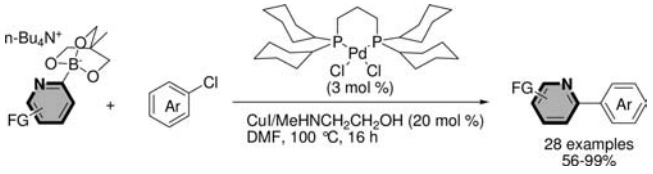
Shohei Sakashita, Miho Takizawa, Juugaku Sugai, Hajime Ito, and Yasunori Yamamoto*

Division of Chemical Process Engineering and Frontier Chemistry Center, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

yasuyama@eng.hokudai.ac.jp

Received June 12, 2013

ABSTRACT



Palladium-catalyzed Suzuki–Miyaura cross-coupling reactions of tetrabutylammonium 2-pyridyltriolborate salts with various aryl (heteroaryl) chlorides can produce the corresponding desired coupling products with good to excellent yields. These tetrabutylammonium salts are more reactive than the corresponding lithium salts. The coupling reactions with aryl chlorides progressed in the presence of $PdCl_2$dcpp (3 mol %) and CuI/$MeNHCH_2CH_2OH$ (20 mol %) in anhydrous DMF without bases.

Suzuki–Miyaura cross-coupling (SMC) reactions provide a powerful and general method for the synthesis of pharmaceuticals and materials.[1] However, SMC reactions under basic aqueous conditions often give undesirable results due to competitive hydrolytic B–C bond cleavage.[2,3] Such cleavage is significantly accelerated by adjacent heteroatoms in boronic acids.[2,4] 2-Pyridylboronic acid derivatives are typical boron compounds that undergo very rapid cleavage with water during coupling reactions. Several approaches for cross-coupling of these conversions to boronic acid derivatives have been reported,[5] including esters such as pinacol organoboronates,[6]

(1) For reviews: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Miyaura, N. In *Advances in Meta-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, 1998; Vol. 6, pp 187–243. (c) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11. (d) Miyaura, N. *J. Organomet. Chem.* **2002**, *653*, 54. (e) Suzuki, A.; Brown, H. C. *Organic Syntheses via Boranes*; Aldrich Chemical Co.: Milwaukee, 2003; Vol. 3. (f) Miyaura, N. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 41–124. (g) Hall, D. G. *Boronic Acids*, 2nd ed.; Wiley-VCH: Weinheim, 2011. (h) Suzuki, A.; Yamamoto, Y. *Chem. Lett.* **2011**, *40*, 894.

(2) (a) Tyrrell, E.; Brookes, P. *Synthesis* **2003**, 469. (b) Campeau, L. C.; Fagnou, K. *Chem. Soc. Rev.* **2007**, *36*, 1058. (c) Hapke, M.; Brandt, L.; Lützen, A. *Chem. Soc. Rev.* **2008**, *37*, 2782.

(3) (a) Ishiyama, T.; Ishida, K.; Miyaura, N. *Tetrahedron* **2001**, *57*, 9813. (b) Fuller, A. A.; Hester, H. R.; Salo, E. V.; Stevens, E. P. *Tetrahedron Lett.* **2003**, *44*, 2935.

(4) (a) Kuiliva, H. G.; Nahabedian, K. V. *Chem. Ind.* **1959**, 1120. (b) Kuivila, H. G.; Nahabedian, K. V. *J. Am. Chem. Soc.* **1961**, *83*, 2164. (c) Nahabedian, K. V.; Kuivila, H. G. *J. Am. Chem. Soc.* **1961**, *83*, 2167. (d) Kuivila, H. G.; Reuwer, J. F., Jr.; Mangravite, J. A. *Can. J. Chem.* **1963**, *41*, 3081. (e) Kuivila, H. G.; Reuwer, J. F., Jr.; Mangravite, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 2666. (f) Brown, R. D.; Buchanan, A. S.; Humffray, A. A. *Aust. J. Chem.* **1965**, *18*, 1521. (g) Fischer, F. C.; Havinga, E. *Recueil* **1974**, *93*, 21. (h) Roques, B. P.; Florentin, D.; Callanquin, M. *J. Heterocycl. Chem.* **1975**, *12*, 195. (i) Florentin, D.; Fournié-Zaluski, M. C.; Callanquin, M.; Roques, B. P. *J. Heterocycl. Chem.* **1976**, *13*, 1265.

(5) (a) Matondo, H.; Souirti, S.; Baboulène, M. *Synth. Commun.* **2003**, *33*, 795. (b) Bouillon, A.; Lancelot, J.-C.; Sopkova de Oliveira Santos, J.; Collot, V.; Bovy, P. R.; Rault, S. *Tetrahedron* **2003**, *59*, 10043. (c) Kinzel, T.; Zhang, Y.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 14073. (d) Ge, S.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 12837. (e) Thakur, A.; Zhang, K.; Louie, J. *Chem. Commun.* **2012**, *48*, 203.

(6) (a) Mkhalid, I. A. I.; Coventry, D. N.; Albesa-Jove, D.; Batsanov, A. S.; Howard, J. A. K.; Perutz, R. N.; Marder, T. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 489. (b) Deng, J. Z.; Paone, D. V.; Ginnetti, A. T.; Kurihara, H.; Dreher, S. D.; Weissman, S. A.; Stauffer, S. R.; Burgey, C. S. *Org. Lett.* **2009**, *11*, 345. (c) Yang, D. X.; Colletti, S. L.; Wu, K.; Song, M.; Li, G. Y.; Shen, H. C. *Org. Lett.* **2009**, *11*, 381. (e) Crowley, B. M.; Potteiger, C. M.; Deng, J. Z.; Prier, C. K.; Paone, D. V.; Burgey, C. S. *Tetrahedron Lett.* **2011**, *52*, 5055. (f) Robbins, D. W.; Hartwig, J. F. *Org. Lett.* **2012**, *14*, 4266.

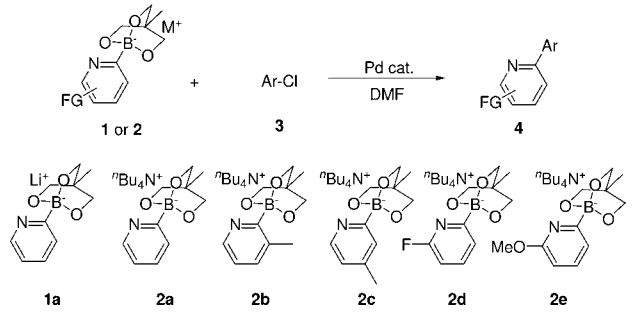
(7) (a) Hodgson, P. B.; Salingu, F. H. *Tetrahedron Lett.* **2004**, *45*, 685. (b) Gros, P.; Doudouh, A.; Fort, Y. *Tetrahedron Lett.* **2004**, *45*, 6239. (c) Gütz, C.; Lützen, A. *Synthesis* **2010**, 85.

(8) (a) Molander, G. A.; Ellis, N. *Acc. Chem. Res.* **2007**, *40*, 275. (b) Darses, S.; Genet, J.-P. *Chem. Rev.* **2008**, *108*, 288. (c) Molander, G. A.; Canturk, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9240.

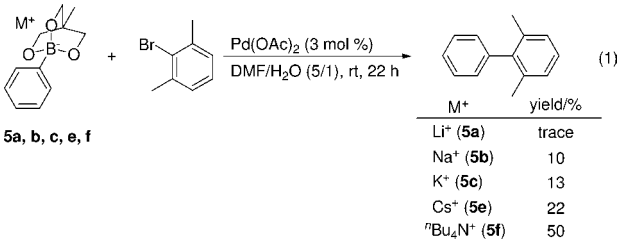
10.1021/ol402268g
Published on Web 08/16/2013

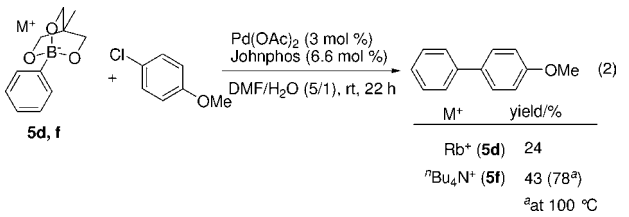
diethanolamine adducts,[7] trifluoroborate salts,[8,9] lithium triisopropoxyborates,[10] and *N*-methyliminodiacetic acid (MIDA) boronates.[11,12] We have developed heteroaryltriolborate salts that are stable for metal-catalyzed reactions.[13−15] Triolborate salts possessing 2-pyridyl, 3-pyridyl, and other heteroarenes afforded biaryls by SMC reactions in high yields at 50−120 °C in anhydrous DMF without bases. There was a strong accelerating effect of copper salts for reactions of 2-pyridyltriolborate derivatives (**1**).[13] However, the coupling of **1** with aryl chlorides (**3**) remains an important and challenging issue. We herein report the cross-coupling of 2-pyridyltriolborates with a wide range of **3** involving electronically deactivated aryl chlorides (Scheme 1). We have already reported that **1** couples in high yield with several aryl bromides and iodides in the presence of a $PdCl_2$dppp and CuI catalyst without bases.[13b,c,g] The yield of SMC reactions of reactive aryl chloride catalyzed by $PdCl_2$dppp and CuI in

Scheme 1. Cross-Coupling of 2-Pyridyltriolborates



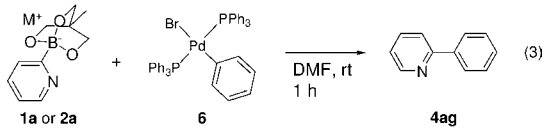
DMF at 80 °C was low. Moreover, electronically and sterically deactivated aryl chlorides tended to react more slowly than their activated ones. To overcome the problem of deactivated aryl chlorides, we considered changing the countercation of pyridyltriolborate.[16] The reaction of phenyltriolborate salt with 2-bromo-*m*-xylene at room temperature shows the following order of reactivity: $^nBu_4N^+ > Cs^+ > K^+ > Na^+ > Li^+$ (eq 1). The tetrabutylammonium salt exhibits a greater accelerating effect. Similarly, in the SMC reaction of phenyltriolborate salt with *p*-anisyl chloride as an electronically deactivated aryl chloride, the tetrabutylammonium salt was more reactive than the rubidium salt (eq 2). *p*-Methoxybiphenyl was obteined finally in 78% yield at 100 °C.

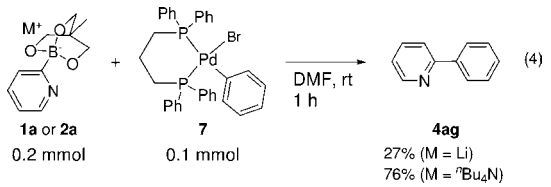




To confirm the influence of countercations on transmetalation, $(Ph_3P)_2Pd(Ph)Br$ (**6**) was reacted with phenyltriolborate salts at room temperature. A difference in reaction rate was observed with the order of efficiency being $^nBu_4N^+ > Cs^+ > K^+ > Li^+$ (Figure 1). Although the lithium salt has been synthetically useful, this has the limitation of being insoluble in an organic solvent such as THF or AcOEt. The tetrabutylammonium salt has the advantage of being readily soluble in THF or AcOEt.

Counterion exchange from lithium to ammonium can be achieved by treating with tetrabutylammonium hydroxide in THF. Next, we tried reactions of lithium and tetrabutylammonium 2-pyridyltriolborate salts with $(Ph_3P)_2Pd(Ph)Br$ (**6**) and dpppPd(Ph)Br (**7**) at room temperature in anhydrous DMF (eqs 3 and 4).





The tetrabutylammonium salt also gave a better yield than that of the lithium salt. As a result, we examined the SMC reaction of tetrabutylammonium 2-pyridyltriolborate salt with aryl chlorides. Unlike the stoichiometric

(9) (a) Molander, G. A.; Biolatto, B. *J. Org. Chem.* **2003**, *68*, 4302. (b) Molander, G. A.; Canturk, B.; Kennedy, L. E. *J. Org. Chem.* **2009**, *74*, 973. (c) Ren, W.; Li, J.; Zou, D.; Wu, Y.; Wu, Y. *Tetrahedron* **2012**, *68*, 1351.

(10) (a) O'Neill, B. T.; Yohannes, D.; Bundesmann, M. W.; Arnold, E. P. *Org. Lett.* **2000**, *2*, 4201. (b) Billingsley, K. L.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4695. (c) Ackermann, L.; Potukuchi, H. K. *Synlett* **2009**, 2852. (d) Haag, B. A.; Sämann, C.; Jana, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2011**, *50*, 7290. (e) Oberli, M. A.; Buchwald, S. L. *Org. Lett.* **2012**, *14*, 4606. (f) Chen, K.; Peterson, R.; Math, S. K.; Lamunyon, J. B.; Testa, C. A.; Cefalo, D. R. *Tetrahedron Lett.* **2012**, *53*, 4873.

(11) Gillis, E. P.; Burke, M. D. *Aldrichimica Acta* **2009**, *42*, 17.

(12) (a) Knapp, D. M.; Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 6961. (b) Dick, G. R.; Knapp, D. M.; Gillis, E. P.; Burke, M. D. *Org. Lett.* **2010**, *12*, 2314. (c) Dick, G. R.; Woerly, E. M.; Burke, M. D. *Angew. Chem., Int. Ed.* **2012**, *51*, 2667.

(13) (a) Yamamoto, Y.; Takizawa, M.; Yu, X.-Q.; Miyaura, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 928. (b) Yamamoto, Y.; Takizawa, M.; Yu, X.-Q.; Miyaura, N. *Heterocycles* **2010**, *80*, 359. (c) Yamamoto, Y.; Sugai, J.; Takizawa, M.; Miyaura, N. *Org. Synth.* **2011**, *88*, 79. (d) Li, G.-Q.; Kiyomura, S.; Yamamoto, Y.; Miyaura, N. *Chem. Lett.* **2011**, *40*, 702. (e) Li, G.-Q.; Yamamoto, Y.; Miyaura, N. *Synlett* **2011**, 1769. (f) Li, G.-Q.; Yamamoto, Y.; Miyaura, N. *Tetrahedron* **2011**, *67*, 6804. (g) Yamamoto, Y. *Heterocycles* **2012**, *85*, 799.

(14) Yu, X.-Q.; Yamamoto, Y.; Miyaura, N. *Chem.—Asian. J.* **2008**, *3*, 1517.

(15) (a) Yu, X.-Q.; Yamamoto, Y.; Miyaura, N. *Synlett* **2009**, 994. (b) Yu, X.-Q.; Shirai, T.; Yamamoto, Y.; Miyaura, N. *Chem.—Asian. J.* **2011**, *6*, 932. (c) Yamamoto, Y.; Takahashi, Y.; Kurihara, K.; Miyaura, N. *Aust. J. Chem.* **2011**, *64*, 1447.

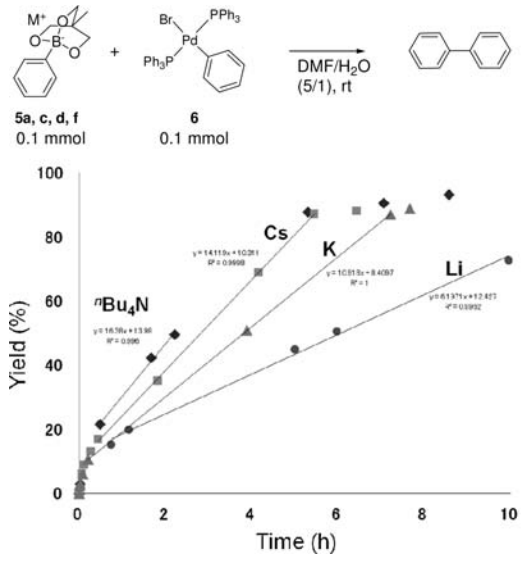
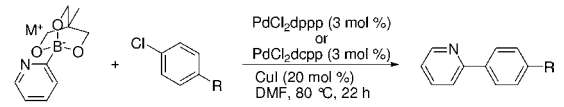


Figure 1. Effect of counterions on transmetalation.

Table 1. Optimization of Cross-Coupling Reactions of 2-Pyridyltriolborate with Aryl Chlorides[a]



1a (M =Li)
2a (M = ^{n}Bu$_4$N)
3a (R = NO_2)
3g (R = H)
4aa (R = NO_2)
4ag (R = H)

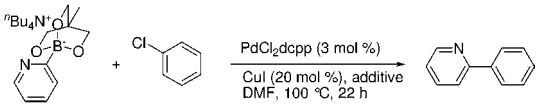
entry	M =	R =	catalyst	additive (mol %)	yield (%)
1	Li	NO_2	$PdCl_2$dppp	none	0
2	**Li**	**NO_2**	**$PdCl_2$dppp**	**CuI (20)**	**57**
3	Li	NO_2	$PdCl_2$dppp	CuBr (20)	45
4	Li	NO_2	$PdCl_2$dppp	CuCl (20)	47
5	**^{n}Bu$_4$N**	**NO_2**	**$PdCl_2$dppp**	**CuI (20)**	**83**
6	Li	H	$PdCl_2$dppp	CuI (20)	0
7	^{n}Bu$_4$N	H	$PdCl_2$dppp	CuI (20)	5
8	^{n}Bu$_4$N	H	$Pd(OAc)_2$/2JohnPhos	CuI (20)	23
9	^{n}Bu$_4$N	H	$Pd(OAc)_2$/2XPhos	CuI (20)	31
10	^{n}Bu$_4$N	H	$PdCl_2$dcpp	CuI (20)	55
11	^{n}Bu$_4$N	H	$PdCl_2$dcpp	CuI (20)	78[b]

[a] Reaction conditions: 2-pyridyltriolborate salt (**1a** or **2a**, 1.25 mmol), aryl chloride (**3**, 0.5 mmol), Pd catalyst (3 mol %), CuI (20 mol %), DMF (3 mL), 80 °C, 22 h. [b] The reaction was carried out at 100 °C.

reactions with palladium bromides, in the catalytic reactions with aryl chlorides, no reaction of the lithium 2-pyridyltriolborate (**1a**) with *p*-nitrochlorobenzene was observed in the absence of CuI (entry 1, Table 1). The addition of catalytic amounts of copper salts such as CuI, CuBr, and CuCl increased the coupling yields to 57%, 45%, and 47%, respectively (entries 2−4). Tetrabutylammonium salt **2a** gave a better yield than that of the lithium salt (57 and 83%, entries 2 and 5). Unfortunately, when the tetrabutylammonium salt was used for reaction with chlorobenzene, the desired products were obtained in only 5% yield (entry 7). Next, we investigated the effects of catalysts. $PdCl_2$dcpp (dcpp = 1,3-bis(dicyclohexylphosphino)propane) gave a 55% yield (entry 10). By further investigations of reaction conditions, 2-phenylpyridine was finally obtained in 78% yield at 100 °C (entry 11).

The role of copper salts seems to be to facilitate the transmetalation of **2a** to arylpalladium chloride by generation of a 2-pyridylcopper species.[6b,12c,17,18] Therefore, we investigated a wide range of ligands for copper iodide (Table 2). As expected, the addition of TMEDA or ethanolamine led to an increase in coupling yield (entries 2−6). *N*-Methyl ethanolamine gave the best yield (95%, entry 6). In examination of the amount of *N*-methyl ethanolamine (entries 6−9), we found that the product was obtained quantitatively by adding 20 mol % (an equivalent amount of copper iodide, entry 9). However, diethylamine provided only 13% yield (entry 10). The yield with the addition of diethanolamine was the same yield as that without diethanolamine (entry 11).

Table 2. Screen of Additives for the Cross-Coupling of 2-Pyridyltriolborate with Chlorobenzene[a]



2a 3g 4ag

entry	additive (equiv)	yield (%)
1	none	78
2	TMEDA (3)	84
3	$H_2NCH_2CH_2OH$ (3)	64
4	$H_2NCH_2CH(CH_3)OH$ (3)	82
5	$BnHNCH_2CH_2OH$ (3)	89
6	$MeHNCH_2CH_2OH$ (3)	95
7	$MeHNCH_2CH_2OH$ (1)	95
8	$MeHNCH_2CH_2OH$ (0.4)	99
9	**$MeHNCH_2CH_2OH$ (0.2)**	**99**
10	$HN(CH_2CH_3)_2$ (3)	13
11	$HN(CH_2CH_2OH)_2$ (3)	77

[a] Reaction conditions: tetrabutylammonium 2-pyridyltriolborate salt (**2a**, 1.25 mmol), chlorobenzene (**3**, 0.5 mmol), $PdCl_2$dcpp (3 mol %), CuI (20 mol %), DMF (3 mL), 100 °C, 22 h.

On the basis of these results, cross-coupling reactions of tetrabutylammonium 2-pyridyltriolborate salts (**2**) with aryl chlorides (**3**) were performed in the presence of $PdCl_2$dcpp (3 mol %) and CuI/$MeHNCH_2CH_2OH$ (20 mol %) in anhydrous DMF at 100 °C. As shown in Table 3, the cross-coupling reactions of **2a** with a series of electron-

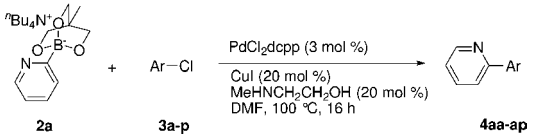
(16) Batey, R. A.; Quach, T. D. *Tetrahedron Lett*. **2001**, *42*, 9099.

(17) (a) Miyaura, N.; Itoh, M.; Suzuki, A. *Tetrahedron Lett*. **1976**, *17*, 255. (b) Miyaura, N.; Sasaki, N.; Itoh, M.; Suzuki, A. *Tetrahedron Lett*. **1977**, *18*, 173. (c) Miyaura, N.; Sasaki, N.; Itoh, M.; Suzuki, A. *Tetrahedron Lett*. **1977**, *18*, 3369. (d) Ichikawa, J.; Minami, T.; Sonoda, T.; Kobayashi, H. *Tetrahedron Lett*. **1992**, *33*, 3779.

(18) (a) Pierrat, P.; Gros, P.; Fort, Y. *Org. Lett*. **2005**, *7*, 697. (b) Mee, S. P. H.; Lee, V.; Baldwin, J. E. *Chem.—Eur. J*. **2005**, *11*, 3294.

withdrawing (entries 1–6) or electron-donating (entries 8–10, 13, 14) para-substituted chloroarenes proceeded in good to excellent yields. In addition, meta- and ortho-substituted aryl chlorides reacted with **2a** in good yield (entries 11, 12, 15, 16).

Table 3. Scope of Cross-Coupling of Tetrabutylammonium 2-Pyridyltriolborate Salt with Aryl Chlorides[a]



2a **3a-p** **4aa-ap**

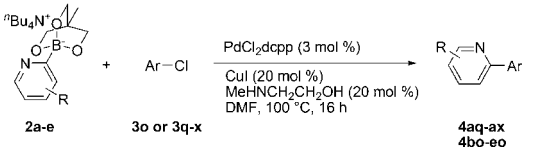
entry	Ar = (**3**)	**4**	yield (%)
1	4-$O_2NC_6H_4$ (**3a**)	**4aa**	93
2	4-NCC_6H_4 (**3b**)	**4ab**	60
3	4-$MeCOC_6H_4$ (**3c**)	**4ac**	66
4	4-$MeO_2CC_6H_4$ (**3d**)	**4ad**	67
5	4-$HOCC_6H_4$ (**3e**)	**4ae**	56
6	4-FC_6H_4 (**3f**)	**4af**	91
7	C_6H_5 (**3g**)	**4ag**	99
8	4-$AcNHC_6H_4$ (**3h**)	**4ah**	62
9	4-$PhOC_6H_4$ (**3i**)	**4ai**	94
10	4-MeC_6H_4 (**3j**)	**4aj**	95
11	3-MeC_6H_4 (**3k**)	**4ak**	90
12	2-MeC_6H_4 (**3l**)	**4al**	79
13	4-^{t}BuC_6H_4 (**3m**)	**4am**	92
14	4-$MeOC_6H_4$ (**3n**)	**4an**	88
15	3-$MeOC_6H_4$ (**3o**)	**4ao**	99
16	2-$MeOC_6H_4$ (**3p**)	**4ap**	74

[a] Reaction conditions: tetrabutylammonium 2-pyridyltriolborate salt (**2a**, 1.25 mmol), chlorobenzene (**3**, 0.5 mmol), PdCl$_2$dcpp (3 mol %), CuI (20 mol %), DMF (3 mL), 100 °C, 22 h.

Cross-coupling between two nitrogen-containing heterobiaryl compounds is challenging, presumably because of the coordinating property of pyridines or bipyridines. As shown in Table 4, we initially studied the coupling of **2a** with 2-chloropyridine derivatives (**3q**, **3r**, and **3s**) or 2-chloroquinoline derivatives (**3t** and **3u**). These reactions generated products with good yields. We presumed that the catalyst is stable because of the chelating property of the dcpp ligand. In coupling with 5-chloro-2-methylbenzo-[d]oxazole (**3v**), this catalytic system showed good reactivity (81%). Utilizing this catalytic system, chloronaphthalenes were also suitable coupling partners as seen in the reactions of **2a** with 1-chloronaphthalene and 2-chloronaphthalene, which resulted in 93% (**4aw**) and 94% (**4ax**) yields, respectively.

Substrates **2**, possessing functional groups, successfully coupled with 3-anisyl chloride (**4bo**–**eo**). The use of 40 mol % CuI/MeNHCH$_2$CH$_2$OH led to an increase in the coupling yield with 3-methyl- (**2b**) and 6-fluoro-2-pyridyltriolborate (**2d**). We further investigated the coupling reaction between 4-methyl-2-pyridyltriolborate (**2c**) and 3-anisyl chloride. This reaction proceeded well to provide the desired products (**4co**) with quantitative yields.

Table 4. Scope of Cross-Coupling of Tetrabutylammonium 2-Pyridyltriolborate Salt with Aryl Chlorides[a]



2a-e **3o or 3q-x** **4aq-ax 4bo-eo**

product	yield (%)	product	yield (%)
4aq	99	**4aw**	93
4ar	85	**4ax**	94
4as	92[b]	**4bo**	77[c]
4at	58	**4co**	99
4au	83	**4do**	64[c]
4av	81	**4eo**	60[d]

[a] Reaction conditions: tetrabutylammonium 2-pyridyltriolborate salt (**2a**, 1.25 mmol), aryl chloride (**3**, 0.5 mmol), PdCl$_2$dcpp (3 mol %), CuI/MeHNCH$_2$CH$_2$OH (20 mol %), DMF (3 mL), 100 °C, 16 h. [b] 2-Chloro-5-nitropyridine (0.5 mmol), lithium 2-pyridyltriolborate salt (1.0 mmol), PdCl$_2$dppp (3 mol %), CuI (20 mol %), NaI (1.0 mmol) in DMF at 80 °C for 22 h. [c] CuI/MeHNCH$_2$CH$_2$OH (40 mol %) were used. [d] NMR yield.

In conclusion, we have newly prepared tetrabutylammonium 2-pyridyltriolborate salts for challenging cross-coupling with aryl (heteroaryl) chlorides. We have developed conditions catalyzed by PdCl$_2$dcpp and CuI/MeNHCH$_2$CH$_2$OH in anhydrous DMF without bases, which provided various 2-arylpyridine derivatives in good to excellent yields.

Acknowledgment. This research was supported in part by *Strategic Molecular and Materials Chemistry through Innovative Coupling Reactions* from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting Information Available. Experimental procedures, preparation of triolborates, spectral data, and spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.