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

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Received June 12, 2013



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 PdCl₂dcpp (3 mol %) and Cul/MeNHCH₂CH₂OH (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

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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

ORGANIC LETTERS

2013 Vol. 15, No. 17

4308-4311

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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 biarvls 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 PdCl₂dppp and CuI catalyst without bases.^{13b,c,g} The yield of SMC reactions of reactive aryl chloride catalyzed by PdCl₂dppp 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

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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 ${}^{n}Bu_4N^+ > Cs^+ > K^+ > Li^+$ (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

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Figure 1. Effect of counterions on transmetalation.

 Table 1. Optimization of Cross-Coupling Reactions

 of 2-Pyridyltriolborate with Aryl Chlorides^a

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$, (M+ 0 0-B-0 +	CI	PdCl₂dppp (3 mol %) or PdCl₂dcpp (3 mol %) Cul (20 mol %) DMF, 80 ℃, 22 h	(3 mol %) (3 mol %) J %) C, 22 h	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1a 2a	(M =Li) (M = ⁿ Bu ₄ N)	3a (R : 3g (R :	= NO ₂) = H)	4aa (R = NO ₂) 4ag (R = H)	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	entry	M =	R =	catalyst	additive (mol %)	yield (%)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1	Li	NO_2	$PdCl_2dppp$	none	0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	Li	NO_2	PdCl ₂ dppp	CuI (20)	57
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	Li	NO_2	PdCl ₂ dppp	CuBr(20)	45
	4	Li	NO_2	PdCl ₂ dppp	CuCl(20)	47
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	${}^{n}\mathbf{Bu_{4}N}$	NO_2	PdCl ₂ dppp	CuI (20)	83
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6	Li	Н	PdCl ₂ dppp	CuI (20)	0
$\begin{array}{llllllllllllllllllllllllllllllllllll$	7	$^{n}\mathrm{Bu}_{4}\mathrm{N}$	н	PdCl ₂ dppp	CuI (20)	5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8	$^{n}\mathrm{Bu}_{4}\mathrm{N}$	Н	Pd(OAc) ₂ /2JohnPhos	CuI (20)	23
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9	$^{n}\mathrm{Bu}_{4}\mathrm{N}$	Н	Pd(OAc) ₂ /2XPhos	CuI (20)	31
11 n Bu ₄ N H PdCl ₂ dcpp CuI (20) 78 ^b	10	$^{n}\mathrm{Bu}_{4}\mathrm{N}$	н	PdCl ₂ dcpp	CuI (20)	55
	11	ⁿ Bu ₄ N	Н	$PdCl_2dcpp$	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. PdCl₂dcpp (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

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

	ⁿ Bu ₄ N'OL OB-O + CI CI CI CI CI	²dCl₂dcpp (3 mol %) Cul (20 mol %), additive DMF, 100 ℃, 22 h		
	2a 3g		4ag	
entry	additiv	e (equiv)	yield (%)	
1	none		78	
2	TMEDA(3)		84	
3	H_2NCH_2CH	$H_2NCH_2CH_2OH(3)$		
4	H_2NCH_2CH	$H_2NCH_2CH(CH_3)OH(3)$		
5	BnHNCH ₂ C	$BnHNCH_2CH_2OH(3)$		
6	$MeHNCH_2O$	$MeHNCH_2CH_2OH(3)$		
7	$MeHNCH_2O$	$MeHNCH_{2}CH_{2}OH(1)$		
8	$MeHNCH_2O$	$2H_{2}OH(0.4)$	99	
9	MeHNCH ₂	CH ₂ OH (0.2)	99	
10	HN(CH ₂ CH	$_{3})_{2}(3)$	13	
11	HN(CH ₂ CH	$_{2}OH)_{2}(3)$	77	

^{*a*} Reaction conditions: tetrabutylammonium 2-pyridyltriolborate salt (**2a**, 1.25 mmol), chlorobenzene (**3**, 0.5 mmol), PdCl₂dcpp (3 mol %), CuI (20 mol %), DMF (3 mL), 100 °C, 22 h.

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).

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 PdCl₂dcpp (3 mol %) and CuI/MeHNCH₂CH₂OH (20 mol %) in anhydrous DMF at 100 °C. As shown in Table 3, the cross-coupling reactions of **2a** with a series of electron-

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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

	ⁿ Bu₄N+OL N→ + Ar−Cl Cul MeH DMF	dcpp (3 mol %) 20 mol %) CM2CH2CH2CH (20 mol %) 100 ℃, 16 h
ontry	$2a \qquad 3a-p$	4aa-ap
entry	AI - (5)	4 yieu (70)
1	$4\text{-}O_2NC_6H_4\left(\boldsymbol{3a}\right)$	4aa 93
2	$4\text{-}\mathrm{NCC}_{6}\mathrm{H}_{4}\left(\mathbf{3b}\right)$	4ab 60
3	$4\text{-MeCOC}_{6}\mathrm{H}_{4}\left(\mathbf{3c}\right)$	4ac 66
4	$4-MeO_2CC_6H_4$ (3d) 4ad 67
5	$4\text{-}HOCC_{6}H_{4}\left(3e\right)$	4ae 56
6	$4\text{-}FC_{6}H_{4}\left(\mathbf{3f}\right)$	4af 91
7	$C_{6}H_{5}\left(\mathbf{3g} ight)$	4ag 99
8	$4\text{-AcNHC}_{6}\text{H}_{4}\left(\mathbf{3h}\right)$	4ah 62
9	$4\text{-PhOC}_{6}\text{H}_{4}\left(3i\right)$	4ai 94
10	$4\text{-MeC}_{6}\text{H}_{4}\left(\mathbf{3j}\right)$	4aj 95
11	$3-MeC_{6}H_{4}\left(\mathbf{3k} ight)$	4ak 90
12	$2 - MeC_6H_4(3l)$	4al 79
13	$4-^{t}BuC_{6}H_{4}\left(\mathbf{3m}\right)$	4am 92
14	$4-MeOC_{6}H_{4}\left(\mathbf{3n}\right)$	4an 88
15	$3-MeOC_{6}H_{4}(\mathbf{3o})$	4ao 99
16	$2\text{-}MeOC_{6}H_{4}\left(\mathbf{3p}\right)$	4ap 74

^{*a*} Reaction conditions: tetrabutylammonium 2-pyridyltriolborate salt (**2a**, 1.25 mmol), chlorobenzene (**3**, 0.5 mmol), PdCl₂dcpp (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 2awith 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/MeNHCH₂CH₂OH 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

Table 4. Scope of Cross-Coupling of Tetrabutylammonium

 2-Pyridyltriolborate Salt with Aryl Chlorides^a





^{*a*} Reaction conditions: tetrabutylammonium 2-pyridyltriolborate salt (**2a**, 1.25 mmol), aryl chloride (**3**, 0.5 mmol), PdCl₂dcpp (3 mol %), CuI/MeHNCH₂CH₂OH (20 mol %), DMF (3 mL), 100 °C, 16 h. ^{*b*} 2-Chloro-5-nitropyridine (0.5 mmol), lithium 2-pyridyltriolborate salt (1.0 mmol), PdCl₂dppp (3 mol %), CuI (20 mol %), NaI (1.0 mmol) in DMF at 80 °C for 22 h. ^{*c*} CuI/MeHNCH₂CH₂OH (40 mol %) were used. ^{*d*} NMR yield.

chloride. This reaction proceeded well to provide the desired products (**4co**) with quantitative yields.

In conclusion, we have newly prepared tetrabutylammonium 2-pyridyltriolborate salts for challenging crosscoupling with aryl (heteroaryl) chlorides. We have developed conditions catalyzed by PdCl₂dcpp and CuI/ MeNHCH₂CH₂OH 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.