



Carbohydrate-based phosphines as supporting ligand for palladium-catalyzed Suzuki–Miyaura cross-coupling reaction



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ABSTRACT

Carbohydrate-based mono-phosphines (**1** and **2**) derived from glucose have been explored as supporting ligand for palladium-catalyzed Suzuki–Miyaura reaction. The combination of phosphine to palladium in a ratio of 2:1 resulted in a longer-living system than that in a ratio of 1:1. Using K_2CO_3 as base, aryl bromides as well as active aryl chlorides can be coupled nearly quantitatively by 0.1–0.2 mol % of **1**/Pd(OAc)₂ with 95–99% of isolated yields. The amount of the catalyst could be lowered to 0.01 mol % under the optimized condition with 80% yield at room temperature. The carbohydrate hydroxyl group in **1** was found to contribute to catalytic activity.

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Metal-catalyzed cross-coupling methodology to form new carbon–carbon and carbon–heteroatom bonds has advanced organic synthesis significantly.¹ The palladium- and nickel-catalyzed coupling of aryl and alkenyl halides (or pseudo halides) with organoboronic acids, known as the Suzuki–Miyaura reaction,² is one of the most widely used methods³ in the synthesis of pharmaceutical compounds,⁴ natural products,⁵ and polymers.⁶ Thanks to the discovery and application of those ligands with electron-rich and sterically demanding characteristics, significant progresses have been witnessed in the last decade.^{7–20}

The phosphine (**1**), (methyl 3-deoxy-4,6-O-phenylmethenyl- α -D-altrropyranosido-3-)-diphenylphosphine, is easily prepared from glucose²¹ and has shown interesting coordination mode to transition metals.^{22–28} The two phenyl groups on phosphorus atom are chemically nonequivalent shown by both of NMR and X-ray diffraction data,²¹ indicating that the steric environment around phosphorus atom is crowded. The altropyrano-ring fusing with another six-member ring creates the highly sterically demanding around the 3-position phosphorus atom, leading to the chemical nonequivalence of the two phenyl groups. Linking to an altropyrano-ring also makes the phosphorus atom electron-richer compared with triphenylphosphine. With the two features of electron-richer and sterically demanding, therefore it is attractive

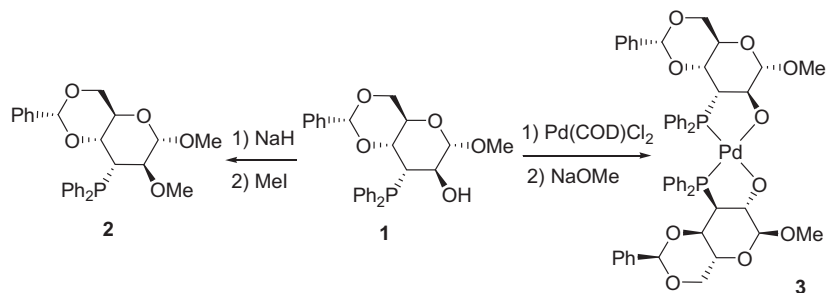
to explore the phosphine **1** as supporting ligand in the palladium-catalyzed Suzuki–Miyaura coupling reactions to enrich ligand library. The carbohydrate-based phosphine for cross-coupling reactions has been explored rarely.^{29,30} Herein we report a highly efficient carbohydrate-based phosphine/palladium system for Suzuki–Miyaura coupling of aryl bromides and active aryl chlorides.

The carbohydrate phosphine **1** is easily accessed through 4 steps from cheap glucose (Scheme 1).²¹ It had been found that the 2-hydroxyl group of altropyranoside in **1** coordinated to palladium(II) under basic condition in dichloromethane at room temperature to form phosphino- and alkoxo-palladium(II) chelate-complex **3** in 86% yield,²⁶ which had been isolated and fully characterized. Since Suzuki–Miyaura reaction is usually conducted under basic condition, the complex **3** can be expected to form especially as the ratio of phosphine to palladium is 2:1. In order to clarify the possible participation of species **3** in catalytic cycle, the 2-hydroxyl group in **1** was masked with methyl to form **2**, methyl 3-deoxy-2-O-2-methyl-4,6-O-phenylmethenyl- α -D-altropyranosido-3-)-diphenylphosphine.

In the initial experiments, the Suzuki–Miyaura reaction was performed between 4-bromotoluene and phenylboronic acid in different solvents with 0.2 mol % of Pd(OAc)₂ using K_2CO_3 as base. It was found that the reaction proceeded smoothly at room temperature in both of THF and 95% ethanol at beginning for the ratio of phosphine to palladium either 1:1 or 2:1. The catalyst system with a ratio of 1:1 stopped after 12 h with the conversion of 4-bromotoluene reaching 80% and 90% (Table 1, entries 1 and 3), respectively in THF

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Scheme 1. Syntheses of carbohydrate-based phosphines and chelate-alkoxopalladium(II) complex.

Table 1
Effect of solvent and temperature on **1**/Pd(OAc)₂-catalyzed Suzuki–Miyaura reaction of 4-bromotoluene with phenylboronic acid^a

Entry	Solvent	Pd/ 1	Temp (°C)	Time (h)	Yield ^b (%)
1	THF	1:1	rt ^c	12	70
				24	80 (75)
2	THF	1:2	rt	12	65
				24	89 (86)
3	95% Ethanol	1:1	rt	12	75
				24	90 (86)
4	95% Ethanol	1:2	rt	12	70
				24	97 (95)
5	Toluene	1:2	rt	12	40
				24	53
6	Acetonitrile	1:2	rt	12	5
				24	5
7	1,4-Dioxane	1:2	rt	12	15
				24	15
8	THF	1:2	73	3	99 (97)
9	95% Ethanol	1:2	88	12	95 (90)
10	Toluene	1:2	123	1	99 (96)
11	Acetonitrile	1:2	90	1	97 (95)
12	1,4-Dioxane	1:2	106	0.2	99 (99)
13	1,4-Dioxane	1:2	106	0.2	99 (99) ^d

^a Reaction conditions: 4-bromotoluene (3.0 mmol), phenylboronic acid (4.5 mmol), Pd(OAc)₂ (0.006 mol), K₂CO₃ (6.0 mmol), solvent (9.0 mL).

^b GLC yield calibrated via dodecane as an internal standard; isolated yields were given in parentheses (average of two runs).

^c 22–32 °C.

^d 0.003 mmol of Pd(OAc)₂.

and 95% ethanol, however the 2:1 ratio system showed a longer-living catalyst and can convert 4-bromotoluene to 97% level with 95% isolated yield of the desired biaryl (entry 4). Suzuki–Miyaura reaction is often needed in pharmaceutical industry, and the reaction carrying out in 95% ethanol at room temperature with mild base such as K₂CO₃ is highly desired.²⁹ These preliminary data showed that the carbohydrate-based phosphine **1** is much better than triphenylphosphine for palladium-catalyzed Suzuki–Miyaura reaction, with the latter as supporting ligand 3–5 mol % of palladium was usually employed.³¹ Besides, with the carbohydrate-based phosphine **1** as supporting ligand the desired reaction condition for pharmaceutical industry upon 0.2 mol % of the palladium loading could be reached. The ratio of 2:1 was chosen and applied for the following exploration of the carbohydrate-based phosphine as supporting ligand for palladium-catalyzed Suzuki–Miyaura reaction. Other solvents such as toluene, acetonitrile, and 1,4-dioxane afforded low conversion of substrate at room temperature (entries 5–7). However, when the reactions were carried out under reflux conditions in the solvents other than 95% ethanol (entry 9), the reactions were completed in a much shorter time, and nearly quantitative conversion with excellent isolated yields was achieved (entries 8, 10–12). It is worthy of notification that the catalyst could be reduced to 0.1 mol % without affecting the reaction time and yield

when the reaction was carried out in refluxing 1,4-dioxane (entry 13).

After optimizing solvent and temperature, various bases were investigated in 95% ethanol. It looked that only K₂CO₃ matched with the solvent of 95% ethanol; other bases tried even such as KOH, Cs₂CO₃, and NaOH were not of choice (Table 2, entries 3, 6, and 8). Although the reason for such a big difference between K₂CO₃ and Cs₂CO₃ as base in 95% ethanol was unclear, that strong base such as NaOH and KOH did not work either might be a clue. On the other hand using 1,4-dioxane as solvent with 0.1 mol % of Pd(OAc)₂, a variety of bases including K₂CO₃, K₃PO₄·3H₂O, KOH, Cs₂CO₃, and NaOH proved to be the choice within 1 h (Table 1, entry 13; Table 2, entries 1, 3, 5, and 7), but around 1% of diphenyl could be observed when using KOH or NaOH as base. The performance of NaOAc was also good although with a longer time (Table 2, entry 9), but the bases Na₂CO₃ and NaOBu-*t* resulted in low yields (entries 11–14).

Since the phosphino- and alkoxy-palladium(II) chelate-complex **3** is easily formed,²⁶ we wondered the complex might participate in the catalytic reaction. Therefore, the hydroxyl-masked phosphine **2** was prepared and tested under the optimized condition to couple 4-bromotoluene with phenylboronic acid. Using **2** as supporting ligand it took 1 h to afford 96% of isolated yield in 1,4-dioxane (Table 3, entry 9), whereas by **1** only 0.2 h of time consumed. In 95% ethanol at room temperature, the difference is slight. These data suggest that the 2-hydroxyl group functions in the catalytic cycle and has the effect to increase the reaction rate. Although it

Table 2
Effect of base on **1**/Pd(OAc)₂-catalyzed Suzuki–Miyaura coupling 4-bromotoluene with phenylboronic acid

Entry	Base	React. Cond. ^a	Time (h)	Yield ^b (%)
1	K ₃ PO ₄ ·3H ₂ O	I	0.2	99 (99)
2	K ₃ PO ₄ ·3H ₂ O	II	24	10
3	KOH	I	0.2	99 (99) ^c
4	KOH	II	24	<5
5	Cs ₂ CO ₃	I	0.2	98 (97)
6	Cs ₂ CO ₃	II	24	13
7	NaOH	I	1	98 (97) ^c
8	NaOH	II	24	<5
9	NaOAc	I	6	94 (90)
10	NaOAc	II	24	10
11	Na ₂ CO ₃	I	6	25
12	Na ₂ CO ₃	II	24	<5
13	NaOBu- <i>t</i>	I	6	<5
14	NaOBu- <i>t</i>	II	24	<5

^a Reaction conditions: aryl halide (3.0 mmol), phenylboronic acid (4.5 mmol), base (6.0 mmol), I or II (I: Pd(OAc)₂ (0.003 mmol), ligand (0.006 mmol), 1,4-dioxane (9 mL), oil bath 106 °C; II: Pd(OAc)₂ (0.006 mmol), ligand (0.012 mmol), 95% ethanol (9 mL), room temperature).

^b GLC yield calibrated via internal standard, isolated yields were given in parentheses (average of two runs).

^c Around 1% of biphenyl was observed.

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