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A highly active palladium-phosphoramidite catalyst for the Suzuki cross-coupling of aryl bromides

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Abstract

A highly efficient palladium-catalyzed Suzuki coupling of aryl bromides with arylboronic acids using phosphoramidite ligand **2c** was developed. The phosphoramidite ligands are cost-effective and easily prepared from inexpensive, commercially available starting materials using a simple, efficient method. It represents an advance toward the discovery of low-cost catalyst systems for eventual availability.

Keywords: Suzuki cross-coupling; Phosphoramidite ligand; Aryl bromide; Palladium

1. Introduction

The palladium-catalyzed Suzuki cross-coupling reactions of aryl halides with arylboronic acids have emerged as an extremely important tool in organic synthesis and great efforts have been made toward the development of efficient catalytic systems for the coupling in the past few years [1]. Among the various palladium-catalyzed systems reported, notably, oxime-carbapalladacycle [2], *N*-heterocyclic carbene [3,4], trivalent oxyphosphorous and aminophosphorous [5], biphenyl-type phosphines [6] and other electron-rich phosphine ligands [7–13] have been proved effective for Suzuki cross-coupling reactions. However, in some cases, the utilization of large amounts of expensive ligands and complicated operations makes the reaction not practical. Thus, cost-effective alternative methods with the use of cheap ligands and simple operation procedures are still needed. For a long run, our group has embarked on a program aimed at the development of ligands that are low-cost and easily prepared in short steps from readily available starting materials. A recent breakthrough has been the development of chiral sulfamide-amine alcohol [14] and oxime-phosphine oxide [15] ligands for the highly enantioselective reactions and *N*-arylation of alkylamines and N–H heterocycles, respectively. In this paper, we applied phenol-based phosphoramidite ligands to palladium-catalyzed Suzuki cross-coupling of aryl bromides with arylboronic acids and disclosed that not only the phosphoramidite ligand **2c** was highly efficient ligand with $Pd(OAc)_2$ as catalyst precursor for the Suzuki cross-coupling but also these phosphoramidite ligands were cost-effective and readily attainable.

2. Experimental

All reactions were carried out under an argon atmosphere and monitored by thin layer chromatography (TLC). Column chromatography purifications were performed using silica gel. All solvents were dried and degassed before use. NMR spectra were measured in $CDCl_3$ on a Bruker DRX-400 NMR spectrometer (400 MHz) with TMS as an internal reference. High resolution mass spectra (HRMS) were recorded on a Mariner 5303 (Applied Biosystems, USA).

2.1. Synthesis of ligands

2.1.1. Typical experimental procedure for the synthesis of *2b*

A dried round-bottomed flask (250 mL) equipped with a motor stirrer, thermometer and dropping funnel was charged with redistilled diethylamine (96.6 mmol) and dried ether (100 mL), and cooled to 0 °C in an ice-water bath under argon. PCl_3 (1.4 mL, 16.1 mmol) in dried ether (50 mL) was added

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dropwise with stirring, during which time a white precipitate was formed. The resulting solution was then allowed to warm slowly to room temperature and stirred overnight. The precipitate was filtered, and the solvent was removed. The residue was dissolved in dried benzene (20 mL) and transferred to a round-bottomed flask (50 mL) equipped with reflux condenser. α-Naphtol (32.2 mmol) and NH_4Cl (0.01 g) were added to the flask and the refluxed mixture was stirred for 6 h under argon. The solvent was removed under reduced pressure. The residue was purified by column chromatography to give a colorless liquid (**2b**) in 90% yield (5.64 g). Others were similar to **2b** in synthesis. **2a**, **2d**–**2f** and **4c** (colorless liquids) were obtained by column chromatography on silica gel with petroleum ether. Crude products of ligands **2c**, **3c** and **5c**–**7c** were purified by recrystallization with ether to afford the desired compounds (white solids).

*2.1.2. Characterization of O,O′-di(α-naphthyl)-N,N-dimethylphosphoramidite (**2a**)*

A colorless liquid (5.12 g, 88% yield). ^{1}H NMR: δ 2.88 (s, 6H), 7.18–7.20 (d, J = 8.0 Hz, 2H), 7.43–7.58 (m, 6H), 7.67–7.69 (d, J = 8.0 Hz, 2H), 7.89–7.95 (t, J = 12.0 Hz, 2H), 8.12–8.14 (d, J = 8.0 Hz, 2H). ^{13}C NMR: δ 35.16, 35.37, 113.52, 113.67, 122.53, 122.93, 125.77, 125.87, 126.53, 127.69, 127.71, 127.77, 135.00, 149.84, 149.91. ^{31}P NMR: δ 144.67. HRMS (APCI) calcd for $C_{22}H_{21}NO_2P$ ($M + H^+$): 362.1290, found 362.1304.

*2.1.3. Characterization of O,O′-di(α-naphthyl)-N,N-diethylphosphoramidite (**2b**)*

A colorless liquid (5.64 g, 90% yield). ^{1}H NMR: δ 1.14–1.18 (t, J = 8.0 Hz, 6H), 3.39–3.47 (m, 4H), 7.17–7.19 (d, J = 8.0 Hz, 2H), 7.17–7.60 (m, 8H), 7.78–7.80 (d, J = 8.0 Hz, 2H), 8.20–8.22 (t, J = 4.0 Hz, 2H). ^{13}C NMR: δ 15.02, 15.06, 38.37, 38.58, 113.33, 113.48, 115.23, 122.43, 122.65, 122.71, 124.39, 125.70, 125.87, 126.24, 126.50, 126.77, 127.77, 135.03, 150.18, 150.24. ^{31}P NMR: δ 140.31. HRMS (APCI) calcd for $C_{24}H_{25}NO_2P$ ($M + H^+$): 390.1597, found 390.1617.

*2.1.4. Characterization of O,O′-di(α-naphthyl)-N,N-di-i-propylphosphoramidite (**2c**)*

A white solid (6.05 g, 90% yield); mp: 122–123 °C. ^{1}H NMR: δ 1.37–1.38 (d, J = 4.0 Hz, 12H), 4.02–4.19 (m, 2H), 7.28–7.36 (m, 4H), 7.47–7.56 (m, 6H), 7.83–7.85 (d, J = 8.0 Hz, 2H), 8.26–8.28 (d, J = 8.0 Hz, 2H). ^{13}C NMR: δ 24.78, 24.84, 44.56, 44.69, 76.89, 77.20, 77.52, 112.89, 113.06, 122.38, 122.71, 124.41, 125.61, 125.91, 126.45, 126.79, 127.76, 135.02, 150.66, 150.72. ^{31}P NMR: δ 142.02. HRMS (APCI) calcd for $C_{26}H_{29}NO_2P$ ($M + H^+$): 418.1904, found 418.1930.

*2.1.5. Characterization of O,O′-di(α-naphthyl)-N,N-dibenzylphosphoramidite (**2d**)*

A colorless liquid (7.67 g, 88% yield). ^{1}H NMR: δ 3.44–3.49 (s, 4H), 7.12–7.18 (t, J = 12.0 Hz, 3H), 7.28–7.32 (t, J = 8.0 Hz, 3H), 7.39–7.52 (m, 12H), 7.76–7.78 (d, J = 8.0 Hz, 3H), 8.20–8.22 (d, J = 8.0 Hz, 3H). ^{13}C NMR: δ 48.18, 48.39, 113.84, 114.00, 122.85, 122.98, 123.28, 124.90, 125.45, 126.03, 126.06, 127.16, 127.33, 128.54, 128.72, 129.05, 129.22, 137.84, 137.86, 150.15, 150.22. ^{31}P NMR: δ 138.01. HRMS (APCI) found for $C_{34}H_{29}NO_2P$ ($M + H^+$): 514.2530.

*2.1.6. Characterization of O,O′-di(α-naphthyl)-N-(1-piperidinyl)phosphoramidite (**2e**)*

A colorless liquid (5.62 g, 87% yield). ^{1}H NMR: δ 1.45–1.61 (m, 6H), 3.30–3.42 (m, 4H), 7.19–7.21(d, J = 8.0 Hz, 2H), 7.31 (s, 2H), 7.43–7.52 (t, J = 16.0 Hz, 6H), 7.76 (s, 2H), 8.22 (s, 2H). ^{13}C NMR: δ 25.10, 27.02, 27.06, 44.62, 44.82, 113.36, 113.51, 122.60, 122.73, 125.69, 125.85, 126.48, 127.76, 135.01, 150.11, 150.17. ^{31}P NMR: δ 135.14. HRMS (APCI) calcd for $C_{25}H_{25}NO_2P$ ($M + H^+$): 402.1646, found 402.1617.

*2.1.7. Characterization of O,O'-di(α-naphthyl)-N-(1-morpholinyl)phosphoramidite (**2f**)*

A colorless liquid (5.62 g, 87% yield). ^{1}H NMR: δ 3.37–3.42 (m, 4H), 3.63–3.75 (m, 4H), 7.19–7.21 (d, J = 8.0 Hz, 2H), 7.30–7.58 (m, 8H), 7.78–7.80 (d, J = 8.0 Hz, 2H), 8.10–8.20 (m, 2H). ^{13}C NMR: δ 43.80, 43.97, 67.71, 67.77, 113.45, 113.61, 115.02, 115.13, 122.29, 123.08, 125.61, 125.74, 126.56, 126.66, 127.41, 127.47, 127.49, 127.71, 127.81, 134.94, 134.96, 149.65, 149.72. ^{31}P NMR: δ 135.71. HRMS (APCI) calcd for $C_{24}H_{23}NO_3P$ ($M + H^+$): 404.1363, found: 404.1370.

*2.1.8. Characterization of O,O′-di(β-naphthyl)-N,N-di-i-propylphosphoramidite (**3c**)*

A white solid (6.12 g, 91% yield); mp: 83–84 °C. ^{1}H NMR: δ 1.26–1.28 (d, J = 8 Hz, 12H), 3.90–3.96 (m, 2H), 7.28–7.30 (d, J = 8.0 Hz, 2H), 7.35–7.37 (d, J = 8.0 Hz, 2H), 7.40–7.43 (t, J = 12.0 Hz, 2H), 7.51 (s, 1H), 7.69–7.78 (m, 6H). ^{13}C NMR: δ 24.60, 24.67, 44.21, 44.35, 121.51, 121.58, 124.44, 124.85, 126.19, 126.43, 127.15, 127.29, 129.49, 129.59, 130.04, 130.49, 134.32, 134.50, 152.18, 152.25. ^{31}P NMR: δ 143.48. HRMS (APCI) calcd for $C_{26}H_{29}NO_2P$ ($M + H^+$): 418.1954, found 418.1930.

*2.1.9. Characterization of O,O′-diphenyl-N,N-di-i-propylphosphoramidite (**4c**)*

A colorless liquid (4.29 g, 84% yield). ^{1}H NMR: δ 1.21–1.23 (d, J = 8 Hz, 12H), 3.81–3.87 (m, 2H), 6.98–7.02 (t, J = 8.0 Hz, 1H), 7.06–7.15 (m, 5H), 7.23–7.32 (m, 4H). ^{13}C NMR: δ 24.52, 24.60, 44.04, 44.18, 119.65, 120.15, 120.24, 120.82, 120.89, 122.75, 123.69, 124.39, 125.44, 128.36, 129.17, 129.51, 129.54, 129.84, 130.02, 154.40, 154.48. ^{31}P NMR: δ 143.49. HRMS (APCI) calcd for $C_{18}H_{25}NO_2P$ ($M + H^+$): 318.1590, found: 318.1617.

*2.1.10. Characterization of O,O′-(1,1′-dinaphthyl-2,2′-diyl)-N,N-di-i-propylphosphoramidite (**5c**)*

A white solid (6.35 g, 95% yield); mp: 174–175 °C. ^{1}H NMR: δ 1.21–1.23 (d, J = 8.0 Hz, 12H), 3.33–3.42 (m, 2H), 7.19–7.31 (m, 4H), 7.39–7.44 (m, 4H), 7.49–7.51 (d, J = 8.0 Hz, 2H), 7.88–7.96 (m, 4H). ^{13}C NMR: δ 24.71, 44.88, 45.00, 122.05, 122.65, 124.43, 124.76, 125.96, 126.06, 127.29, 128.36,

128.44, 129.51, 130.33, 130.67, 131.47, 132.90, 133.00, 150.38. ^{31}P NMR: δ 152.00. HRMS (APCI) calcd for $C_{26}H_{27}NO_2P$ ($M+H^+$): 416.1748, found 416.1774.

2.1.11. Characterization of O,O′-(1,1′-diphenyl-2,2′-diyl)-N,N-di-i-propylphosphoramidite (6c)

A white solid (4.67 g, 92% yield); mp: 79–80 °C. ^{1}H NMR: δ 1.21–1.23 (d, J = 8 Hz, 12H), 3.48–3.54 (m, 2H), 7.17–7.22 (m, 4H), 7.31–7.34 (t, J = 8.0 Hz, 2H), 7.44–7.46 (d, J = 8.0 Hz, 2H). ^{13}C NMR: δ 24.57, 24.65, 44.67, 44.80, 122.27, 124.31, 129.06, 129.84, 131.03, 152.05, 152.09. ^{31}P NMR: δ 152.26. HRMS (APCI) calcd for $C_{18}H_{23}NO_2P$ ($M+H^+$): 316.1447, found 316.1461.

2.1.12. Characterization of O,O′-(o-diphenyl)-N,N-di-i-propylphosphoramidite (7c)

A white solid (3.20 g, 83% yield); mp: 70–71 °C. ^{1}H NMR: δ 1.21–1.23 (d, J = 8 Hz, 12H), 3.31–3.37 (m, 2H), 6.83–6.85 (m, 2H), 6.92–6.95 (m, 2H). ^{13}C NMR: δ 24.66, 24.74, 45.16, 45.29, 119.03, 120.27, 122.86, 147.15, 147.23. ^{31}P NMR: δ 156.01. HRMS (APCI) calcd for $C_{12}H_{19}NO_2P$ ($M+H^+$): 240.1134, found 240.1148.

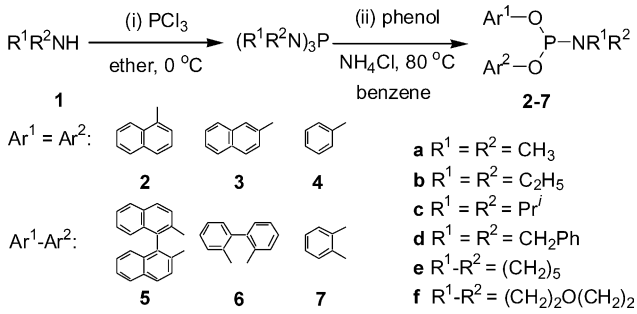
2.2. General procedure for palladium-catalyzed Suzuki cross-coupling reaction

Arylboronic acid (1.5 mmol) and K_3PO_4 (638 mg, 3 mmol) were added to a screw-capped test tube. The tube was then evacuated and backfilled with argon (five cycles). Pd $(OAc)_2$ (0.11 mg, 0.0005 mmol), ligand **2c** (0.42 mg, 0.001 mmol), aryl bromide (1.0 mmol) and dioxane (1 mL) were added at room temperature. The tube was then charged with argon and sealed with screw-capped. The reaction mixture was stirred at 80 °C for 12 h. The reaction mixture was then allowed to room temperature. Ethyl acetate (4 mL) and water (10 mL) were added. The reaction mixture was further extracted with ethyl acetate (4 × 10 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. Solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel to afford the desired product.

3. Results and discussion

As shown in Scheme 1, the phosphoramidite ligands **2**–**7** were easily synthesized in high yields from the inexpensive, commercially available amines, PCl_3 and corresponding phenols by simple two steps. All ligands were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS and known ligands compared with the previously reported literature [16]. The experiments have shown that not only these ligands for solid were obtained by recrystallization rather than using complex column chromatography but also they were also stable.

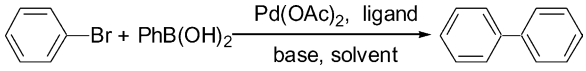
In our search for optimal reaction conditions, the $Pd(OAc)_2$-catalyzed cross-coupling of bromobenzene with phenylboronic acid was employed as the model reaction using ligand **2c** at 80 °C. The choice of bases and solvents is usually important in



Scheme 1. Synthesis of phosphoramidite ligands.

achieving an efficient cross-coupling reaction. Therefore, different solvents and bases were screened and the results are summarized in Table 1. The widely used solvents such as DMSO, DMF, toluene, dioxane, THF and CH_3CN had remarkable effect on the coupling reaction, while dioxane was the best among the solvents (entries 1–6). A brief survey was carried out to determine the influence of the bases with dioxane as solvent which showed that the model reaction could be conducted with highest efficiency using K_3PO_4 as base (entries 6–14). We believed that the bases used in entries 7–10 are strong enough to decompose the catalyst when the reaction occurs and probably palladium

Table 1
Optimization studies for Suzuki cross-coupling[a],



Entry	Ligand	Base	Solvent	Yield (%)[b]
1	**2c**	K_3PO_4	DMSO	16
2	**2c**	K_3PO_4	DMF	43
3	**2c**	K_3PO_4	Toluene	90
4	**2c**	K_3PO_4	CH_3CN	17
5[c]	**2c**	K_3PO_4	THF	87
6	**2c**	K_3PO_4	Dioxane	98
7	**2c**	$KOBu^t$	Dioxane	9
8	**2c**	$NaOBu^t$	Dioxane	19
9	**2c**	$LiOBu^t$	Dioxane	41
10	**2c**	KOH	Dioxane	58
11	**2c**	K_2CO_3	Dioxane	93
12	**2c**	Cs_2CO_3	Dioxane	16
13	**2c**	NEt_3	Dioxane	20
14[d]	**2c**	–	Dioxane	8
15	**2a**	K_3PO_4	Dioxane	3
16	**2b**	K_3PO_4	Dioxane	3
17	**2d**	K_3PO_4	Dioxane	36
18	**2e**	K_3PO_4	Dioxane	2
19	**2f**	K_3PO_4	Dioxane	3
20	**3c**	K_3PO_4	Dioxane	52
21	**4c**	K_3PO_4	Dioxane	19
22	**5c**	K_3PO_4	Dioxane	21
23	**6c**	K_3PO_4	Dioxane	20
24	**7c**	K_3PO_4	Dioxane	3

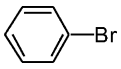
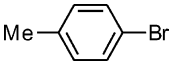
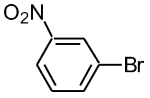
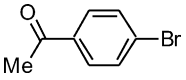
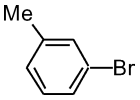
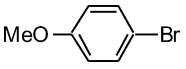
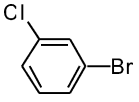
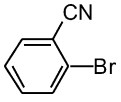
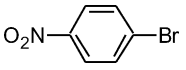
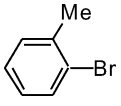
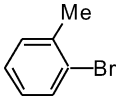
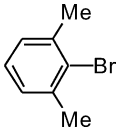
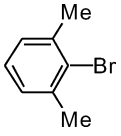
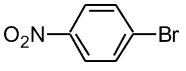
[a] Reaction was carried out with 1.0 mmol of bromobenzene, 1.5 mmol of $PhB(OH)_2$ and 3.0 mmol of base in 1 mL of solvent. 0.05 mol% of $Pd(OAc)_2$ was used as the catalyst precursor with 0.10 mol% of ligand, at 80 °C in 12 h under argon.

[b] Isolated yields (average of two runs).

[c] Reaction was carried out at 66 °C.

[d] No base was used.

Table 2
Suzuki cross-coupling of aryl bromides with aryl boronic acids using **2c**[a], $ArBr + Ar'B(OH)_2 \xrightarrow[K_3PO_4]{Pd(OAc)_2,\ \mathbf{2c}} Ar{-}Ar'$

Entry	ArBr	Pd loading (mol%)	Yield (%)[b]	TON
1		0.05	98	1960
2		0.05	97	1940
3		0.01	99	9900
4		0.01	>99	9900
5		0.05	97	1940
6		0.05	93	1860
7		0.05	95	1900
8		0.01	>99	9900
9		0.01	>99	9900
10		0.05	72	1400
11		0.1	94	940
12		0.05	70	1400
13		0.1	92	920
14[c]		0.05	>99	1980

[a] Reaction was carried out with 1.0 mmol of aryl bromide, 1.5 mmol $PhB(OH)_2$ and 3.0 mmol of K_3PO_4 at 80 °C in 1 mL of dioxane under argon in 12 h. Pd/**2c** = 1:2.
[b] Isolated yields (average of two runs).
[c] 4-$MeOC_6H_4B(OH)_2$ was employed instead of $PhB(OH)_2$.

black is formed during the reaction. Certainly, the bases should not be too weak which almost could not prompt the reactions (entries 7–14).

With the above-mentioned optimal results, a variety of phosphoramidites with different structures were further used for the coupling of bromobenzene with phenylboronic acid (entries 15–24). Unexpectedly, both the phenol moiety and the alkyl groups linking to nitrogen of ligands had very remarkable influence on the coupling reaction. The best result with 98% yield was obtained using **2c** as ligand (entry 6).

The catalytic system of $Pd(OAc)_2$/**2c**/K_3PO_4 with dioxane as solvent was further extended to other representative aryl bromide substrates bearing different functional groups with excellent yields being obtained in the reaction with phenylboronic acid (Table 2, entries 1–9). A wide range of functional groups was tolerated in the reaction. Sterically hindered 2-bromotoluene and 2,6-dibromotoluene also could be coupled with phenylboronic acid to afford products in high yields (entries 10–13). The representative 4-methoxylphenylboronic acid also gave high yield of the reaction (entry 14). Obviously, it can be seen that $Pd(OAc)_2$/**2c** system was indeed highly efficient with low Pd-loading and relatively high turnover numbers toward Suzuki cross-coupling and could tolerate a variety of functional groups including both "deactivating" electron-donating substituents and sterically encumbering *ortho*-substituents on the aryl bromides.

4. Conclusion

In summary, we have developed a highly efficient palladium-catalyzed Suzuki coupling of aryl bromides with arylboronic acids using phosphoramidite ligands. The ligands are cost-effective and easily synthesized from inexpensive, commercially available starting materials using a simple, efficient method. Although this catalytic system is restricted to the coupling of aryl bromides with arylboronic acids, these favorable characteristics make this protocol of potentially practical utility accessible in many cases and represent an advance toward the discovery of simplified catalyst systems for eventual availability.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2005.08.031.

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