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Graphical Abstract

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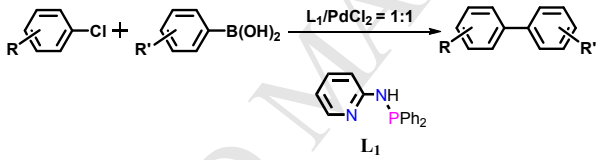

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Suzuki-Miyaura cross-coupling reaction of aryl chlorides with aryl boronic acids catalyzed by a palladium dichloride adduct of N-diphenylphosphanyl-2-aminopyridine

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ABSTRACT

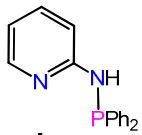
One palladium dichloride adduct of a phosphine-pyridine ligand N-diphenylphosphanyl-2-aminopyridine (**L**$_1$) [(**L**$_1$)PdCl$_2$] (**1**) has been prepared and structurally characterized. Compound **1** can be used as an effective catalyst for the Suzuki-Miyaura cross-coupling reactions of unreactive aryl chlorides with aryl boronic acids, and worked much better than its mono- or bidentate phosphine ligands. The reactions with a wide scope of substrates proceeded to give desired products in good to excellent yields.

1. Introduction

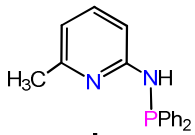
There have been major efforts in the past decades to develop efficient catalysts for the Suzuki–Miyaura cross-coupling reaction.[1,2] The most important topic in this respect has been the structure of the reactive palladium intermediates involved in the key transmetalation step.[3] Relative to aryl bromides and iodides as substrates, aryl chlorides are less expensive, less toxic and less wasteful. While aryl bromides and iodides in the Suzuki-Miyaura coupling reactions work well, their chloride analogues generally go less reactive and require harsher conditions and/or longer reaction times to give the coupling products in lower yields. Thus the development of catalysts that can efficiently activate aryl chlorides remains a big challenge.[4] Over years, researchers have introduced electron-withdrawing groups into aryl chlorides to achieve their reactivity. However, reports on examples of high yields usually involve aryl chlorides with the strong electron-withdrawing nitro and cyano groups.[5] The activation of aryl chlorides is still quite tough for those containing the electron-neutral alkyl, medium electron-withdrawing acyl, aldehyde groups and electron-neutral/-donating groups.[6]

Since Gregory C. Fu first published a catalytic system for the activation of aryl chlorides in Suzuki-Miyaura reaction in 1998,[7] many research groups including Kwong,[8] Buchwald,[9] Sarkar,[10] Hong,[11] Lee,[12] and Rajabi[13] have developed various catalyst candidates. Modifications on ligands include bulky or electron-rich phosphines,[14] nitrogen-donors,[15] N-heterocyclic carbenes[16] and other ligands[17] capable of increasing the electron density at palladium and thereby accelerating the oxidative addition step in the catalytic cycle.[18]

Unlike these homo-donor chelate ligands, hetero-donor ligands have a distinct *trans* effect which can play an pertinent role in controlling activity and selectivity.[19] The synthesis and catalytic activity of complexes bearing hemi-labile ligands of the types P,N[20] and P,O[21] have been widely reported. P- and N- donor ligands bearing large groups are of interest because of their ability to stabilize transition metal catalysts.[22] Besides, the π-acceptor ability of the phosphine can stabilize a metal center in a low oxidation state, while the nitrogen σ-donor makes the metal center more susceptible to oxidative addition reactions.[23] Thus, the hetero-bidentate P,N-donor ligands represent an important class of ligands that have been explored in various catalytic systems, but not extensively in the Suzuki–Miyaura reaction.[24, 25]



L$_1$



L$_2$

In our previous report,[6i] we successfully designed a N,P,P ligand, N,N-bis-(diphenylphosphanylmethyl)-2-aminopyridine (bdppmapy), and prepared its $PdCl_2$ adduct [(bdppmapy)$PdCl_2$].

This catalyst showed good activity toward the Suzuki-Miyaura coupling reactions of aryl bromides and arylboronic acids in ethanol, but showed poor performance in catalyzing the similar reactions using aryl chlorides. As an extension of this project, we deliberately selected two P,N type bidentate ligands N-phenylphosphanylmethyl-2-aminopyridine (**L_1**) and N-phenylphosphanylmethyl-2-amino-6-methylpyridine (**L_2**), and prepared one $PdCl_2$ adduct [(**L_1**)$PdCl_2$] (**1**). Compound **1** exhibited good catalytic activity toward the Suzuki-Miyaura cross-coupling reaction of aryl chlorides with aryl boronic acids. Described below are its synthesis, structural characterization and catalytic performance.

2. Results and discussion

Treatment of $PdCl_2$ with equimolar **L_1** in DMF followed by a standard workup produced yellow crystals of [(**L_1**)$PdCl_2$] (**1**). Compound **1** is relatively stable in air, and soluble in polar solvents such as DMF, DEF, and DMSO, but only slightly soluble in other common solvents such as CH_2Cl_2, EtOH and H_2O. Single-crystal X-ray analysis revealed that **1** crystallizes in the monoclinic space group $P2_1/c$. The Pd(II) center is coordinated by a P atom and a N atom from one **L_1** molecule and two chlorides, forming a *cis* square-planar geometry (Fig. 1). The mean Pd-Cl bond length of **1** are comparable to those of the square planar-coordinated Pd(II) complexes.[6a, 26] The powder X-ray diffraction (PXRD) patterns of the bulky sample of **1** are consistent with the simulated patterns generated from the single crystal data of **1** (Fig. S1). The IR spectrum showed one stretching vibration at 1435 cm^{-1} attributable to the C-P groups of **L_1**. The ^1H NMR spectrum of **1** (Fig. S2) in DMSO-d_6 showed the signals for the –Ph groups (7.91–7.04 ppm) and pyridine ring (10.13-9.03 ppm). One signal at 77.8 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum (Fig. S4). The TGA measurement (Fig. S5) indicated that **1** is quite stable at 200 °C, which eliminates **L_1** molecule at 200–365 °C (59.6%, Calcd 59.0%) and two chlorides at 365-650 °C (13.9%, Calcd 15.1%) to leave PdO as a residual species (26.5%, Calcd 25.9%).

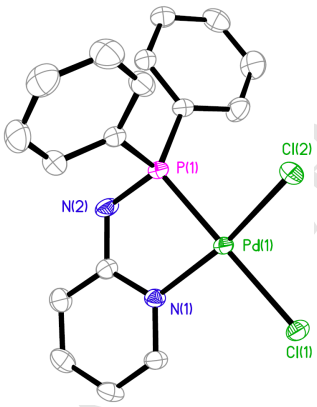


Fig. 1. View of the crystal structure of **1**. All H atoms are omitted for clarity. Selected bond lengths (Å): Pd(1)-Cl(1) 2.3844(6), Pd(1)-Cl(2) 2.2801(6), Pd(1)-N(1) 2.0543(18), Pd(1)-P(1) 2.1802(6).

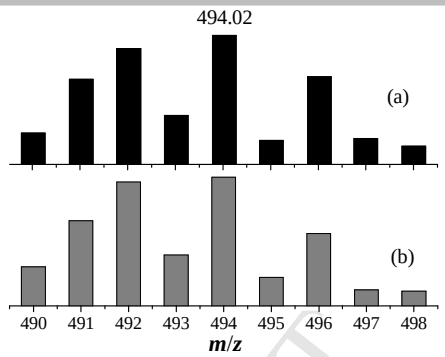
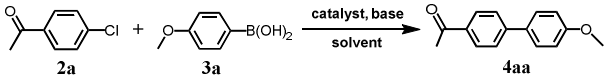


Fig. 2. The positive-ion ESI mass spectrum (a) and the calculated isotope patterns (b) of the $[L_1/PdCl\cdot DMF]^+$ cation.

4-Chloroacetophenone (**2a**) and 4-methoxy phenylboronic acid (**3a**) were chosen as model substrates. The positive-ion ESI mass spectrum of **1** in DMF was examined and provided an insight into its solution behavior. A major signal at m/z = 494.02 (Fig. S6) could be assigned to the $[(L_1)PdCl\cdot DMF]^+$ cation (Fig. 2). The presence of this cation indicated that Pd^{2+} and **L_1** remain coordinated in solution, while one Pd-Cl bond is likely to be broken in solution, which is helpful in inserting the Pd atom into the C-Cl bond of aryl chloride during the oxidative addition step in the catalytic cycle.[18]

The effects of different phosphine ligands were initially evaluated (Table 1). Reaction without any ligands for the cross-coupling of 4-chloroacetophenone (**2a**) with 4-methoxy-phenylboronic acid (**3a**) generated the coupled product (**4aa**) in 36% yield under these conditions (entry 1). The yield was significantly decreased in the presence of monodentate triphenylphosphine (entry 2). Similarly, addition of bidentate phosphine ligands such as dppm, dppe, dppp in this system reduced this yield with the exception of dppf and one POP ligand Xantphos (entries 3-7). The participation of P,N ligand **L_1** led to a higher yield (entry 8). In order to evaluate the influence of steric effects in this catalytic system, we prepared another P,N ligand N-phenylphosphanylmethyl-2-amino-6-methylpyridine (**L_2**). Notably, the increasing hindrance at the 6-position of the pyridine ring in **L_2** resulted in a significant decrease in activity (entry 9). This result is contrary to those reported using P,N palladium catalysts,[27] but similar to that observed using other pyridine-based ligands.[28] The reason may be attributed to the weak axial steric hindrance of pyridine and the reduced basicity of the pyridine nitogen.[29] Thus, these P,N-donor ligands possess one weakly coordinating group that may yield an unsaturation at the Pd(II) center via Cl dissociation.

Table 1 The effect of different phosphine ligands on the Suzuki-Miyaura cross-coupling reaction.



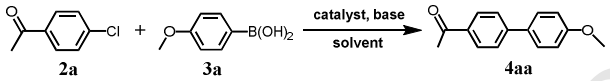
Entry	Catalyst system	Yield (%)
1	$PdCl_2$	36
2	$PdCl_2$ / PPh_3	9
3	$PdCl_2$ / dppm[a]	35
4	$PdCl_2$ / dppe[b]	31

5	$PdCl_2$ / dppp[c]	13	5	THF	65	6
6	$PdCl_2$ / dppf[d]	43	6	DMF	60	34
7	$PdCl_2$ / Xantphos[e]	62	7	DMF	80	51
8	$PdCl_2$ / **L_1**	78	8	DMF	100	55
9	$PdCl_2$ / **L_2**	31	9	DMF	120	52

Reaction conditions: **2a** (1 mmol), 3**a** (1.5 mmol), $K_3PO_4 \cdot 3H_2O$ (3 mmol), DMF (5 mL), $PdCl_2$/**L** = 1/1, catalyst loading (2 mol% Pd), 18 h, 100 °C, analyzed by GC, average of two runs. [a]dppm = bisdiphenylphosphinomethane; [b]dppe = 1,2-bis(diphenylphosphino)ethane; [c]dppp = 1,3-bis(diphenylphosphino) propane; [d]dppf = 1,1'-bis(diphenylphosphino)ferrocene; [e]Xantphos = dimethylbisdiphenylphosphinoxanthene

The influences of bases, solvents and temperatures on this coupling reaction were then investigated (Table 2). Potassium phosphate (2 mmol) had a better effect on the yield of the desired product (entry 3) than KOH and K_2CO_3 (entries 1 and 2), and exhibited a slight improvement with an increased amount (3 mmol, entry 4). The yields were surprisingly poor in toluene, water, ethanol or THF as a solvent at each boiling point (EtOH and THF) or as high as 100 °C (entries 1-5 in Table 3), but got increased in DMF at 60 °C or above (entries 6-9). However, reactions in DMF reached the best yield at 100 °C (entry 8), but did not go well at higher temperature (entry 9). This phenomenon was probably due to the partly decomposition of **L_1** after the long-term reactions.[30]

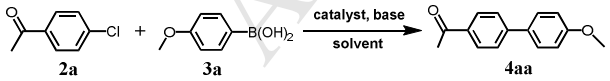
Table 2 The effect of different bases on the Suzuki-Miyaura cross-coupling reaction.



Entry	Base / amount	Yield (%)
1	KOH / 2 mmol	23
2	K_2CO_3 / 2 mmol	22
3	$K_3PO_4 \cdot 3H_2O$ / 2 mmol	41
4	$K_3PO_4 \cdot 3H_2O$ / 3 mmol	52

Reaction conditions: **2a** (1 mmol), **3a** (1.5 mmol), DMF (3 mL), $PdCl_2$/**L_1** = 1/1, catalyst loading (2 mol% Pd), 120 °C, 24 h, analyzed by GC, average of two runs.

Table 3 The effect of solvents and temperatures on the Suzuki-Miyaura cross-coupling reaction.

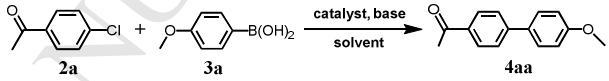


Entry	Solvent	Temperature (°C)	Yield (%)
1	Dioxane	100	18
2	Toluene	100	9
3	H_2O	100	8
4	EtOH	78	7

Reaction conditions: **2a** (1 mmol), **3a** (1.5 mmol), Solvent (3mL), $K_3PO_4 \cdot 3H_2O$ (3 mmol), $PdCl_2$/**L_1** = 1/1, catalyst loading (2 mol% Pd), 24 h, analyzed by GC, average of two runs.

Interestingly the concentration of substrate can influence the yields of the desired products. As listed in Table 4, the highest yield of 83% was found at a concentration of 0.2 mol/L (entry 3) for 4-chloroacetophenone (**2a**) when it was adjusted from 0.10 to 0.30 mol/L (entries 1-5). Enlarged reaction by doubling all reactants and solvent to keep the concentration being 0.2 mol/L gave a similar yield (entry 6). This result might be caused by a balance between speeding up the main and side reactions at higher concentrations and slowing down the reactions due to the insolubility of excess inorganic base.

Table 4 The effect of substrate concentrations on the Suzuki-Miyaura cross-coupling reaction.

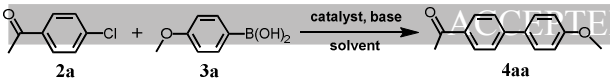


Entry	Ar-Cl (mol/L)	Yield (%)
1	0.10	60
2	0.15	63
3	0.20	83
4	0.25	60
5	0.30	55
6[a]	0.20	82

Reaction conditions: **2a** (1 mmol), **3a** (1.5 mmol), $K_3PO_4 \cdot 3H_2O$ (3 mmol), DMF (5 mL), $PdCl_2$/**L_1** = 1/1, catalyst loading (1.5 mol% Pd), 100 °C, 15 h, analyzed by GC, average of two runs. [a] aryl halide (2 mmol), arylboronic acid (3 mmol), $K_3PO_4 \cdot 3H_2O$ (6 mmol), DMF (10 mL), catalyst loading (3 mol% Pd).

Investigation on the lower limit of the catalyst loading and reaction time revealed that the majority of electron-poor substrate 4-chloroacetophenone (**2a**) was converted into the desired product using 2 mol% palladium catalyst for 24 h at 100 °C (Table 5, entry 1), and no starting materials were detected. Decreasing the catalyst loading and the reaction time to 1.5 mol% and 18 h, respectively, made no difference (entry 2). Similarly, a yield of 83% was still obtained in the presence of 1.5 mol% catalyst after 15 h (entry 3), but reduced to 59% at a reaction time of 12 h (entry 4). Returning the time to 15 h and reducing the loading to 1 mol% improved the yield (74%) (entry 5). Thus, the reaction conditions were optimized as follows: 5 mL DMF, 1 mmol aryl halides, 1.5 mmol arylboronic acid, 3 mmol $K_3PO_4 \cdot 3H_2O$, $PdCl_2$/**L_1** = 1/1 with 1.5 mol% Pd loading, 100 °C and 15 h.

Table 5 The effect of reaction time and catalyst loadings on the Suzuki-Miyaura cross-coupling reaction.

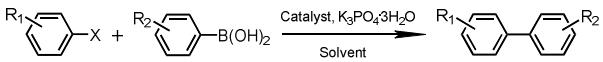


Entry	catalyst loading (mol% Pd)	Time (h)	Yield (%)
1	2.0	24	81
2	1.5	18	82
3	1.5	15	83
4	1.5	12	59
5	1.0	15	74

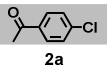
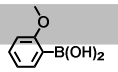
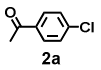
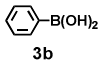
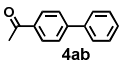
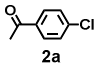
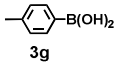
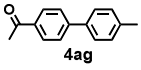
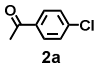
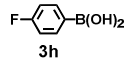
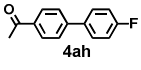
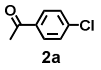
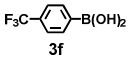
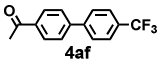
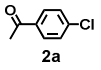
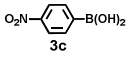
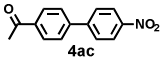
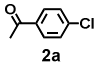
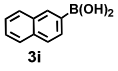
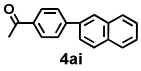
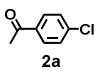
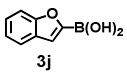
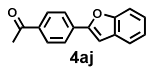
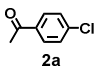
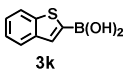
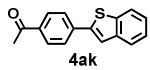
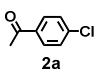
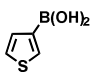
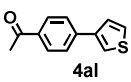
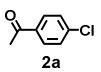
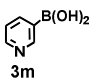
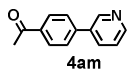
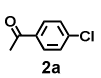
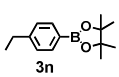
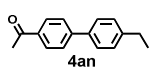
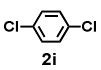
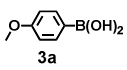
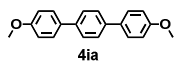
Reaction conditions: **2a** (1 mmol), **3a** (1.5 mmol), $K_3PO_4 \cdot 3H_2O$ (3 mmol), DMF (5 mL), $PdCl_2/\mathbf{L_1}$ = 1/1, 100 °C, analyzed by GC, average of two runs.

Under the optimized conditions, the reactions of a wide range of electronically diverse substrates were examined (Table 6). Aryl chlorides with electron-withdrawing substituents including 4-chloroacetophenone (**2a**), 3-chloroacetophenone (**2b**), 2-chloroacetophenone (**2c**), *p*-chlorotrifluoromethylbenzene (**2d**), *m*-chlorotrifluoromethylbenzene (**2e**), *p*-chlorobenzyl cyanide (**2f**), *p*-chlorobenzaldehyde (**2g**) and *p*-chloronitrobenzene (**2h**) underwent coupling with 4-methoxyphenylboronic acid (**3a**) to afford the desired biaryls in good yields (82-98%, entries 1-8). Substituted aryl chlorides exerted steric effect on the desired products. The *meta*-substituted aryl chlorides **2b** and **2e** (entries 3 and 5) gave similar yields to those obtained from the *para*-substituted ones **2a** and **2d** (entries 1 and 4), while *ortho*-substituted one **2c** produced a slightly lower yield (entry 3). On the other hand, by comparing the *para*-substituted aryl chlorides, it seems that the electron-withdrawing capacity of substituents was positive correlated to the yields in the following order $-NO_2 > -CF_3 > -CN > -CHO \approx -COCH_3$ (entries 8, 4, 6, 7 and 1, respectively). This phenomenon was consistent with that reported in other Suzuki-Miyaura reactions.[4a] In contrary, the reactions of the electron-neutral chlorobenzene (**2i**) and 2-chloropyridine (**2j**) (entries 9 and 10) and the electron-donating *p*-chloroanisole (**2k**) (entry 11) afforded the related products in less yields (10-53%). The reactions between *p*-chloroanisole (**2k**) and electron-neutral/donating phenylboronic acids produced trace or no product (entries 12 and 13). Steric effects of the phenylboronic acids did not work well in this system (entries 14, 15, 18 and 19). Strong electron-withdrawing *p*-chloronitrobenzene (**2e**) showed excellent reactivity (85-98% yields) despite the boronic acids were substituted by electron-donating (entries 8, 14 and 15), electron-neutral (entry 16) and even electron-withdrawing (entry 17) groups. Therefore we selected the medium electron-withdrawing *p*-chloroacetophenone (**2a**) to intensively explore the electron effects of the boronic acids. The yields of the corresponding products were acceptable in the cases of electron-donating (entries 1, 18, 19) and electron-neutral (entries 20 and 21) phenylbronic acids, but gradually dropped when introducing a series of electron-withdrawing –F, $-CF_3$ and $-NO_2$ groups (entries 22-24). The reactions also gave good yields for the naphtylboronic acid and benzoheteroaromatic boronic acids (entries 25-27), but went inactive when using single heteroaromatic boronic acids (entries 28-29) and 4-ethylphenylboronic acid pinacol ester (entry 30). However, as chloride is electron-donating, double arylation using *p*-dichlorobenzene (**2i**) with 4-methoxyphenylboronic acid (**3a**) resulted the 4,4"-dimethoxy-1,1':4',1"-terphenyl (**4ia**) in relatively low but reasonable yield (46%, entry 31). Compared to the reported results using N-heterocyclic carbene as ligand, this catalytic system generally acquired comparable coupling efficiency.[6b-d] Nevertheless, our catalytic efficiency appears to exhibit higher yields and wider scope of substrates than other catalytic systems.[6e-k, 24f]

Table 6 Substrate scope of the Suzuki-Miyaura coupling of aryl chlorides with arylboronic acids



Entry	ArX	Ar'B(OH)$_2$	Product	Yield (%)
1	2a	3a	4aa	85
2	2b	3a	4ba	86
3	2c	3a	4ca	82
4	2d	3a	4da	95
5	2e	3a	4ea	96
6	2f	3a	4fa	93
7	2g	3a	4ga	86
8	2h	3a	4ha	98
9	2i	3a	4ia	10[a]
10	2j	3a	4ja	23
11	2k	3a	4ka	53
12	2k	3b	4ia	trace
13	2k	3c	4ea	NR
14	2h	3d	4hd	92
15	2h	3e	4he	96
16	2h	3b	4hb	95
17	2h	3f	4hf	85
18	2a	3d	4ad	77

19	 2a	 3e	 4ae	81
20	 2a	 3b	 4ab	81
21	 2a	 3g	 4ag	80
22	 2a	 3h	 4ah	78
23	 2a	 3f	 4af	56
24	 2a	 3c	 4ac	37
25	 2a	 3i	 4ai	63
26	 2a	 3j	 4aj	80
27	 2a	 3k	 4ak	81
28	 2a	 3l	 4al	trace
29	 2a	 3m	 4am	trace
30	 2a	 3n	 4an	NR
31[b]	 2i	 3a	 4ia	46

Reaction conditions: aryl chlorides (1 mmol), arylboronic acid (1.5 mmol), $K_3PO_4 \cdot 3H_2O$ (3 mmol), DMF (5 mL), $PdCl_2$/**L_1** = 1/1, catalyst loading (1.5 mol% Pd), 100 °C, 15 h, isolated yield, average of two runs. [a] GC yield. [b] aryl halides (1 mmol), arylboronic acid (3 mmol), $K_3PO_4 \cdot 3H_2O$ (6 mmol), DMF (10 mL), catalyst loading (3 mol% Pd).

3. Conclusions

In summary, we have synthesized one mononuclear complex **1** from reaction of $PdCl_2$ with a P,N bidentate ligand **L_1** and employed **1** as a catalyst for the Suzuki-Miyaura cross-coupling reaction of aryl chlorides and aryl boronic acids. This catalytic system is suitable for a wide scope of substrates and remarkably better than mono- and bi-dentate phosphines under the same conditions. Relative to the similar catalytic system using the bulky analogue **L_2**, complex **1** proved very effective for the coupling reactions of the relatively unreactive aryl chlorides containing strong and medium electron-withdrawing groups. The results demonstrate the importance of ligand design for stabilizing low-valence Pd intermediates and the advantage in incorporating both a π-acceptor P and σ-donor N into the chelating ligands.

4. Experimental

4.1. General procedures

All manipulations were carried out using standard Schlenk techniques. The ligands **L_1** and **L_2** were prepared according to literature procedures.[31] The substrates and other chemicals used for the experiments were purchased from commercial suppliers. GC analyses were performed on an Agilent 7820A Gas Chromatograph with an Agilent HP-5 chromatographic column and N_2 as mobile phase. Thermogravimetric analysis (TGA) was performed on a TASDT Q600 System (heating rate of 10 °C min^{-1}, under an air stream of 100 mL min^{-1}). The LC-MS analyses were recorded in a Rapid Resolution HT-3 chromatographic column on an Agilent 1260 Infinity Liquid Chromatograph with 6120 Quadrupole Mass Spectrometer and MeCN as the mobile phase. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on Varian UNITYplus-300, 400 and 600 spectrometers with chemical shifts referenced to residual solvent signal. The powder X-ray diffraction (PXRD) measurements were carried out on a PANalytical X'Pert PRO MPD system (PW3040/60). Electrospray ion mass spectra (ESI-MS) were performed on micrOTOF-Q III mass spectrometer.

4.2. Synthesis of compound 1

$PdCl_2$ (0.0089 g, 0.05 mmol) and **L_1** (0.0139 g, 0.05 mmol) were added to a Schlenk tube containing a magnetic stirrer bar, and then DMF (5 mL) was added. The mixture was stirred for 12 h at room temperature to provide a yellow solution. Some yellow block crystals of **1** were obtained by volatilization from the yellow solution at room temperature after several days, which were collected by filtration, washed with Et_2O and dried *in vacuo*. Yield: 0.0171 g, 75%. Anal. Calcd. for $C_{17}H_{15}Cl_2N_2PPd$ (%): C, 44.81; H, 3.32; N, 6.15; Found (%): C, 44.77; H, 3.56; N, 6.16. IR (KBr disk, cm^{-1}): 3462(m), 3078(m), 2919(w), 2839(w), 2768(w), 1610(vs), 1477(vs), 1466(vs), 1435(s), 1385(m), 1307(w), 1275(w), 1234(w), 1157(m), 1105(s), 1023(w), 998(w), 902(s), 880(w), 783(m), 745(m), 705(s), 687(s), 625(w), 534(s), 488(s), 479(s). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 10.13 (s, 1H), 9.04 (d, J = 5.9 Hz, 1H), 7.88 (dd, J = 13.3, 7.7 Hz, 5H), 7.68 (dd, J = 28.6, 6.1 Hz, 6H), 7.15 (d, J = 8.3 Hz, 1H), 7.05 (t, J = 6.6 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6, ppm): 161.9, 161.8, 149.0, 142.1, 133.4, 133.0, 132.9, 129.6, 129.5, 116.7, 111.7, 111.6. ^{31}P{^{1}H} NMR (243 MHz, DMSO-d_6, ppm): δ 77.8.

4.3. X-ray structure determination

Single crystals suitable for X-ray analysis were obtained from the above preparation and mounted in a capillary. Diffraction intensities were collected on a Bruker D8-Quest using graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. The program *APEX2* v2012.4-3 (Bruker, AXS) was used for the refinement of cell parameters and the reduction of collected data, while absorption corrections (multi-scan) were applied. The crystal structure of **1** was solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXL-2013 program package.[32] All non-H atoms were refined anisotropically. All H atoms were placed in geometrically idealized positions. A summary of key crystallographic information is given in Table 7.

Table 7 Crystal data and structure refinement parameters for compound **1**

Formula	$C_{17}H_{15}Cl_2N_2PPd$
Formula weight	455.58
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.6676(15)
b/Å	11.6312(14)
c/Å	24.346(3)
β/°	103.503(3)

V/Å^3	3488.0(7)
D_c/g.cm^{-3}	1.735
Z	8
μ(Mo-K_α)/mm^{-1}	1.461
F(000)	1808
Total Reflections	85023
Unique Reflections	8681
No. observations	6607
No. parameters	415
R_{int}	0.0359
R^a	0.0259
wR^b	0.0636
GOF^c	1.067

$^aR = ||F_o|-|F_c||/|F_o|$. $^bwR = \{w(F_o^2-F_c^2)^2/w(F_o^2)^2\}^{1/2}$. ^{c}GOF= $\{w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

4.4. General procedure for the Suzuki-Miyaura cross-coupling reaction of aryl chlorides with aryl boronic acids

In a 25 mL Schlenk tube containing a magnetic stirrer bar, 4-chloroacetophenone (**2a**) (155 mg, 1 mmol) was mixed with 4-methoxyphenylboronic acid (**3a**) (228 mg, 1.5 mmol). Then trihydrate potassium phosphate (798 mg, 3 mmol) and DMF (5 mL) were added. The dissolved mixture of **1** (1.50 mL, 0.015 mmol) was transferred into the tube by a pipette. The tube was placed in a 100 °C oil bath and stirred for 15 h. At the end of the reaction, the mixture was cooled to room temperature, added with water (5 mL), and then extracted with ethyl acetate (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was subjected to silica gel column chromatography to give the cross-coupling product. Finally, the resulting products were characterized using ^{1}H NMR and ^{13}C NMR. See Supplementary data for full ESI-MS data of the catalysts and characterization data for the isolated products.

*4.4.1. 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone (**4aa**).*[33] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.00 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 3.86 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 197.8, 160.0, 145.5, 135.4, 132.4, 129.1, 128.4, 126.7, 114.5, 55.5, 26.7.

*4.4.2. 1-(4'-methyl-[1,1'-biphenyl]-3-yl)ethan-1-one (**4ba**).*[34] Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.14 (s, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.65 – 7.42 (m, 3H), 7.00 (d, J = 8.3 Hz, 2H), 3.86 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 198.3, 159.7, 141.4, 137.7, 132.8, 131.4, 129.1, 128.3, 126.7, 126.6, 114.5, 55.5, 26.9.

*4.4.3. 1-(4'-methyl-[1,1'-biphenyl]-2-yl)ethan-1-one (**4ca**).*[34] Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.50 (dd, J = 15.9, 7.6 Hz, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 6.96 (d, J = 8.3 Hz, 2H), 3.85 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): 205.4, 159.7, 141.0, 140.2, 133.1, 130.8, 130.1, 127.9, 127.2, 114.3, 55.4, 30.5.

*4.4.4. 4-trifluoromethyl-4'-methoxy-1,1'-biphenyl (**4da**).*[37] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.65 (s, 4H), 7.54 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 159.9, 144.4, 132.3, 128.4, 127.8, 126.9, 125.8 (d, J_{CF} = 3.7 Hz), 124.5 (d, J_{CF} = 271.8 Hz), 114.5, 55.5.

*4.4.5. 3-trifluoromethyl-4'-methoxy-1,1'-biphenyl (**4ea**).*[37] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.78 (s, 1H), 7.71 (d, J = 7.1 Hz, 1H), 7.61 – 7.46 (m, 4H), 6.99 (d, J = 8.3 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 159.8, 141.7, 132.3, 131.2 (d, J_{CF} = 32.0 Hz), 130.0, 129.3, 128.4, 125.3, 123.5 (m, J_{CF} = 3.7 Hz), 114.5, 55.5.

*4.4.6. 4-cyano-4'-methoxy-1,1'-biphenyl (**4fa**).*[34] White solid, ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.86 (q, J = 8.3 Hz, 4H), 7.72 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 160.3, 145.3, 132.6, 131.6, 128.4, 127.2, 119.1, 114.6, 110.2, 55.5.

*4.4.7. 4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (**4ga**).*[35] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 10.03 (s, 1H), 7.92 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.7, 160.0, 146.6, 134.5, 131.9, 130.2, 128.4, 126.9, 114.3, 55.3.

*4.4.8. 4-methoxy-4'-nitro-1,1'-biphenyl (**4ha**).*[33] Yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 8.26 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 160.5, 147.3, 146.6, 131.1, 128.6, 127.2, 124.2, 114.7, 55.5.

*4.4.9. 2-(4-methoxyphenyl)-pyridine (**4ja**).*[33] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.66 (s, 1H), 7.96 (s, 2H), 7.74–7.65 (m, 2H), 7.18 (d, J = 4.0 Hz, 1H), 7.00 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 160.5, 157.2, 149.6, 136.7, 132.1, 128.2, 121.5, 119.9, 114.2, 55.4.

*4.4.10. 4,4'-Dimethoxy-1,1'-biphenyl (**4ka**).*[33] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47 (d, J = 8.6 Hz, 4H), 6.96 (d, J = 8.6 Hz, 4H), 3.84 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

*4.4.11. 3-methoxy-4'-nitro-1,1'-biphenyl (**4hd**).*[34] Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.29 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 7.41 (t, J = 7.9 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.14 (s, 1H), 6.99 (d, J = 6.8 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): 160.1, 147.5, 147.1, 140.2, 130.2, 127.8, 124.0, 119.8, 114.1, 113.2, 55.4.

*4.4.12. 2-methoxy-4'-nitro-1,1'-biphenyl (**4he**).*[36] Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.25 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.4 Hz, 1H), 7.01 – 7.09 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): 156.4, 146.6, 145.4, 130.6, 130.3, 1301, 128.2, 123.2, 121.1, 111.4, 55.5.

*4.4.13. 4-nitro-1,1'-biphenyl (**4eb**).*[5(b)] Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.30 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 7.4 Hz, 2H), 7.48 (dt, J = 14.4, 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 147.8, 147.2, 138.9, 129.3, 129.1, 128.0, 127.5, 124.3.

*4.4.14. 4-trifluoromethyl-4'-nitro-1,1'-biphenyl (**4hf**).*[37] Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.34 (d, J = 8.6 Hz, 2H), 7.75 (dd, J = 11.2, 7.6 Hz, 6H). ^{13}C NMR (151 MHz, DMSO-d_6, ppm): δ 147.7, 146.0, 142.2, 128.1, 127.8, 126.1 (d, J_{CF} = 3.6 Hz), 124.2, 123.9 (d, J_{CF} = 273.3 Hz).

*4.4.15. 1-(3'-methoxy-[1,1'-biphenyl]-4-yl)ethanone (**4ad**).*[38] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.02 (d, J = 7.9 Hz, 2H), 7.68 (d, J = 7.9 Hz, 2H), 7.39 (t, J = 7.8 Hz, 1H), 7.22 – 7.15 (m, 2H), 6.95 (d, J = 7.7 Hz, 1H), 3.88 (s, 3H), 2.64

(s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 197.7, 160.0, 145.6, 141.3, 136.0, 130.0, 128.8, 127.2, 119.7, 113.5, 113.1, 55.3, 26.6.

*4.4.16. 1-(2'-methoxy-[1,1'-biphenyl]-4-yl)ethanone (**4ae**).*[34] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.00 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.38-7.32 (q, 2H), 7.07-6.99 (m, 2H), 3.82 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 197.8, 156.4, 143.6, 135.5, 130.7, 129.7, 129.5, 128.0, 120.9, 111.3, 55.5, 26.6.

*4.4.17. 1-([1,1'-Biphenyl]-4-yl)ethan-1-one (**4ab**).*[33] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 (d, J = 8.1 Hz, 2H), 7.66 (dd, J = 23.0, 7.8 Hz, 4H), 7.47 (t, J = 7.4 Hz, 2H), 7.41 (d, J = 7.2 Hz, 1H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 197.8, 145.9, 140.0, 136.0, 129.1, 129.0, 127.4, 26.8.

*4.4.18. 1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (**4ag**).*[39] White solid, ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.02 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 2.60 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 196.9, 144.9, 137.4, 136.1, 134.8, 128.8, 128.1, 126.2, 126.1, 25.8, 20.3.

*4.4.19. 1-(4'-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (**4ah**).*[37] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 (d, J = 8.0 Hz, 2H), 7.66 – 7.57 (m, 4H), 7.16 (t, J = 8.5 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 197.7, 163.1 (d, J_{CF} = 248.1 Hz), 144.8, 136.1 (d, J_{CF} = 3.1 Hz), 135.9, 129.1 (d, J_{CF} = 2.8 Hz), 127.2, 116.0 (d, J_{CF} = 21.6 Hz), 26.7.

*4.4.20. 1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (**4af**).*[37] White solid, ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.08 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.88 (dd, J = 16.7, 8.1 Hz, 4H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, ppm): δ 197.5, 142.8, 136.4, 129.0, 127.9, 127.3, 125.9 (d, J_{CF} = 3.8 Hz), 124.2 (d, J_{CF} = 272.0 Hz), 26.8.

*4.4.21. 1-(4'-nitro-[1,1'-biphenyl]-4-yl)ethan-1-one (**4ac**).*[40] Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm):δ 8.34 (d, J = 7.3 Hz, 2H), 8.09 (d, J = 7.0 Hz, 2H), 7.76 (dd, J = 21.9, 7.3 Hz, 4H), 2.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 197.9, 147.9, 146.5, 143.4, 137.3, 129.4, 128.4, 124.5, 116.0, 27.0.

*4.4.22. 1-(4-(Naphthalen-1-yl)phenyl)ethan-1-one (**4ai**).*[41] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.08 (d, J = 8.7 Hz, 3H), 7.96–7.86 (m, 3H), 7.79 (dd, J = 22.8, 7.8 Hz, 3H), 7.52 (d, J = 3.6 Hz, 2H), 2.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 197.9, 145.8, 137.3, 136.0, 133.7, 133.1, 129.1, 128.8, 128.5, 127.8, 127.6, 126.7, 126.6, 126.5, 125.3, 26.8.

*4.4.23. 1-(4-(Benzofuran-2-yl)phenyl)ethan-1-one (**4aj**).*[42] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.06–8.00 (m, 2H), 7.94 (t, J = 6.0 Hz, 2H), 7.66–7.50 (m, 2H), 7.38–7.22 (m, 2H), 7.17 (d, J = 5.2 Hz, 1H), 2.64 (d, J = 5.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 197.4, 155.3, 154.6, 136.6, 134.7, 129.0, 125.3, 124.9, 123.4, 121.4, 111.5, 103.8, 26.7.

*4.4.24. 1-(4-(Benzo[b]thiophen-2-yl)phenyl)ethan-1-one (**4ak**).*[43] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.01 (d, J = 8.2 Hz, 2H), 7.83 (dd, J = 19.6, 7.9 Hz, 4H), 7.67 (s, 1H), 7.37 (t, J = 5.5 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 197.3, 142.6, 140.4, 139.9, 138.7, 136.4, 129.0, 126.3, 125.0, 124.8, 124.0, 122.3, 121.2, 26.6.

*4.4.25. 4,4''-dimethoxy-1,1':4',1''-terphenyl (**4ia**).*[44] White solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.61 (s, 4H), 7.57 (d, J = 8.0 Hz, 4H), 7.01-6.98 (d, J = 12.0 Hz, 4H), 3.86 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 159.1, 139.1, 133.3, 128.0, 127.0, 114.2, 55.4.

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Supplementary data

The ^{1}H and ^{13}C NMR spectra for the isolated products can be found in online version at http://dx.doi.org/10.1016/*******。 CCDC **** contain the supplementary crystallographic data of compound **1** can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Research Highlights

► Compound **1** is a $PdCl_2$ adduct of N-diphenylphosphanyl-2-aminopyridine.

► Compound **1** can catalyze the reactions of aryl chlorides with aryl boronic acids.

► This catalytic system is suitable for a wide scope of substrates.