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Preparation of a cobalt-containing P,N-bidentate ligand ligated palladium complex: Its applications in amination and Suzuki cross-coupling reactions

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ABSTRACT

A cobalt-containing P,N-ligand, alkyne-bridged dicobalt phosphine $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4(\mu,\eta\text{-}Me_2NCH_2C{\equiv}CP(Cy)_2)]$ (**4c**), was prepared from the reaction of $Me_2NCH_2C{\equiv}CPR_2$ (**2c**) with a dppm-bridged dicobalt complex $[Co_2(CO)_6(\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2)]$ (**3**). Further reaction of **4c** with $Pd(COD)Cl_2$ gave a **4c**-chelated palladium dichloride complex $(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4(\mu,\eta\text{-}Cy_2PC{\equiv}CCH_2NMe_2)\text{-}\ PdCl_2$ (**5c**). Compound **5c** was characterized by spectroscopic methods and crystal structure of **5c** was determined by single-crystal X-ray diffraction techniques. It shows that **4c** is an authentic cobalt-containing P,N-bidentate ligand. Amination and Suzuki reactions employing either a **4c**/palladium salt system or an isolated **5c** as the catalytic precursor led to satisfactory results.

1. Introduction

Transition metal complexes catalyzed cross-coupling reactions, assisted by ligands, are doubtless the most utilized means for making the C–X (X = C, N, O, S, . . .) bonds in modern synthetic chemistry [1–7]. As demonstrated repeatedly, a well-chosen ligand is essential to the success of the coupling reaction [8]. Up to now, there are five categories of ligands listed as the most frequently used: (a) bis(diphenylphosphino)alkyl; (b) trialkylphosphine; (c) aryldialkylphosphine; (d) palladacycle; (e) *N*-heterocyclic carbine. Among them, phosphines remain as the most commonly employed ligands in the catalytic reactions mediated by ligand-assisted transition metals [9–12,8,13–31]. Bidentate phosphines have been found particularly crucial to the reductive elimination process, the last step, of a catalytic cycle of the common cross-coupling reactions. At least there are two advantages of employing bidentate phosphine ligand: first, the enforced *cis*-form of the metal complex by the bidentate ligand enhances the rate of reductive elimination process; second, an undesired side reaction, β-hydride elimination, might be avoided due to less room left for the process. Two of the most representative homofunctional bidentate phosphines are BINAP [32] and DPPF [33]. The former is a typical organic phosphine; the letter is the most cited metal-containing phosphine. Recently, the subject of employing hybrid ligand [34] such as P,N-bidentate ligand, which contains both P- and N-coordination sites, in the complexation of transition metal has attracted attention from many researchers [35–43]. The advantages of employing hybrid ligand are obvious. On the one hand, the P,N-bidentate ligand is less air-sensitive than di-phosphine; on the other, the ready formation/breaking of the nitrogen–metal bond in the metal complex is a profitable feature in catalytic reaction [44,45]. According to the HSAB theory, the chemical bonding is thermodynamically unfavorable for the hard base (nitrogen) and the soft acid (palladium) [46–48].

Our previous works had shown that several cobalt-containing P,N-ligands, alkyne-bridged dicobalt phosphines $[(\mu\text{-}PPh_2CH_2PPh_2)\text{-}Co_2(CO)_4(\mu,\eta\text{-}Me_2NCH_2C{\equiv}CPR_2)]$ (**4a**: R = ^{t}Bu; **4b**: R = Ph; **4c**: R = Cy), could be prepared from the reactions of a dppm-bridged dicobalt complex $[Co_2(CO)_6(\mu\text{-}PPh_2CH_2PPh_2)]$ **3** with corresponding alkynylphosphines $Me_2NCH_2C{\equiv}CPR_2$ (**2a**: R = ^{t}Bu; **2b**: R = Ph; **2c**: R = Cy) (Scheme 1) [49].

An attempt to prepare **4a**-chelated palladium dichloride complex $(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4(\mu,\eta\text{-}Ph_2PC{\equiv}CCH_2NMe_2)PdCl_2$ (**5a**) or *trans*-$[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4(\mu,\eta\text{-}Ph_2PC{\equiv}CCH_2NMe_2)]_2\text{-}PdCl_2$ (**6a**), from the newly made P,N-ligand **4a** with $PdCl_2$ was not successful (Scheme 1). Rather, the reaction of **4a** with another palladium source, $[(\eta^3\text{-}C_3H_5)PdCl]_2$, yielded an unusual **4a**-chelated palladium complex ion pair $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4(\mu,\eta\text{-}Ph_2PC{\equiv}CCH_2NMe_2)Pd(\eta^3\text{-}C_3H_5)]^+[(\eta^3\text{-}C_3H_5)PdCl_2]^-$ (**7a**). Here, **4a** is an authentic cobalt-containing P,N-bidentate ligand [49]. Satisfactory efficiencies were observed for the amination reactions of aryl bromides with morpholine employing either a **4a**-chelated palladium complex composed *in situ* or pre-formed **7a** as the catalytic precursor [49].

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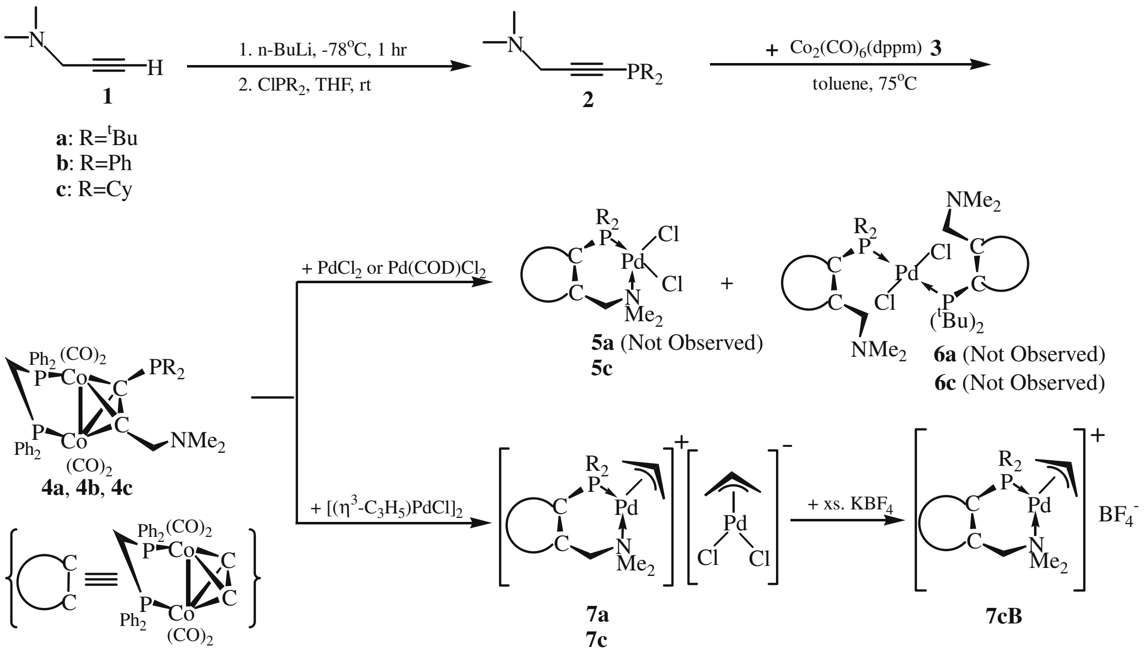


Scheme 1.

The electronic and steric characteristics of a substituent such as electron-withdrawing/donating capacity and bulkiness of a phosphine ligand are two crucial factors that affect the performance of a catalytic reaction [10,21,11,12,8,13,50,51,15–20]. Two frequently employed electron-donating and bulk groups, $-^{t}$Bu and –Cy, are among the most efficient substituents. More than often, the catalytic performance of the former is better than the latter [52–63]. In comparison with the catalytic efficiency of the **4a**-chelated palladium complex, the **4c** ligated palladium complex is prepared and its capability as an effective catalyst precursor either in Suzuki or amination reaction is presented.

2. Results and discussion

2.1. Complexation of **4c** with palladium sources

The preparation of cobalt-containing P,N-ligand **4c** was demonstrated elsewhere [49]. The **4c**-chelated palladium dichloride complex (μ-PPh$_2$CH$_2$PPh$_2$)Co$_2$(CO)$_4$(μ,η-Cy$_2$PC$\equiv$CCH$_2$NMe$_2$)PdCl$_2$ (**5c**) can be prepared by the reaction of the newly made P,N-ligand **4c** with PdCl$_2$, a commonly used palladium source, under 60 °C (Scheme 1). Alternatively, **5c** could be obtained easily by the reaction of **4c** with Pd(COD)Cl$_2$ at 25 °C for only 10 min. Compound **5c** was characterized by spectroscopic methods as well as single-crystal X-ray diffraction techniques (Table 1). In the ^{1}H NMR spectrum of **5c**, one set of quantet shows up at 3.70 ppm which is corresponding to the methylene protons of the coordinated dppm ligand. A singlet observed at 3.41 ppm is assigned to the methylene adjacent to nitrogen. The ^{31}P NMR spectrum displays two singlets at 38.8 and 49.3 ppm. The former signal is assigned to the 2 equiv. phosphorus atoms of the coordinated dppm ligand; while the latter peak is assigned to the palladium-coordinated phosphorus site. It is a significant shift from the free phosphorus in **4c** which appears at 15.11 ppm. The ORTEP diagram of **5c** are depicted in Fig. 1. As revealed in **5c**, **4c** behaves as a conventional cobalt-containing P,N-bidentate ligand. The palladium center is in a square planar environment. There are methanol molecules encapsulated during the crystal growing process. The reaction of **4c** with a different palladium source, [(η^3-C$_3$H$_5$)PdCl]$_2$, resulted in **7a**-related compound, **7c**. In the excess KBF$_4$, a unique **4c**-chelated palladium complex ion pair [(μ-dppm)Co$_2$(CO)$_4$(μ,η-Ph$_2$PC$\equiv$CCH$_2$NMe$_2$)Pd(η^3-C$_3$H$_5$)]$^+$-[BF$_4$]$^-$ **7cB** was yielded. The two chlorides in **5c** are subjected to the replacement of other suitable substituents.

Table 1
Crystal data of **5c**.

Compound	**5c**
Formula	$C_{47}H_{52}Cl_2Co_2NO_5P_3Pd$
Formula weight	1071.02
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	14.449(2)
b (Å)	11.7700(18)
c (Å)	15.824(2)
α (°)	90.00
β (°)	111.942(3)
γ (°)	90.00
V (Å^3)	2496.1(6)
Z	2
D_{calc} (Mg/m^3)	1.462
λ (Mo Kα) (Å)	0.71073
μ (mm^{-1})	1.260
θ Range (°)	1.52–26.07
Observed reflections ($F > 4\sigma(F)$)	9446
Number of refined parameters	545
[a]R_1 for significant reflections	0.0487
[b]wR_2 for significant reflections	0.1003
[c]Goodness-of-fit	0.937

[a] $R_1 = |\Sigma(|F_o| - |F_c|)/|\Sigma F_o||$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 0.0500$ for **5c**.
[c] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

Selected bond distances (Å) and angles (°): Pd(1)–P(3) 2.241(2); Pd(1)–N(1) 2.180(7); Pd(1)–Cl(1) 2.296(2); Pd(1)–Cl(2) 2.425(2); P(3)–C(1) 1.766(8); P(3)–C(12) 1.833(9); P(3)–C(6) 1.840(8); N(1)–C(5) 1.494(10); N(1)–C(3) 1.494(10); N(1)–C(4) 1.495(10); C(1)–C(2) 1.766(8); C(2)–C(3) 1.498(12); N(1)-Pd(1)–Cl(1) 170.70(19); P(3)–Pd(1)–Cl(1) 85.34(9); N(1)–Pd(1)–P(3) 97.51(18); N(1)–Pd(1)–Cl(2) 89.97(19); P(3)–Pd(1)–Cl(2) 169.25(9); Cl(1)–Pd(1)–Cl(2) 88.49(9).

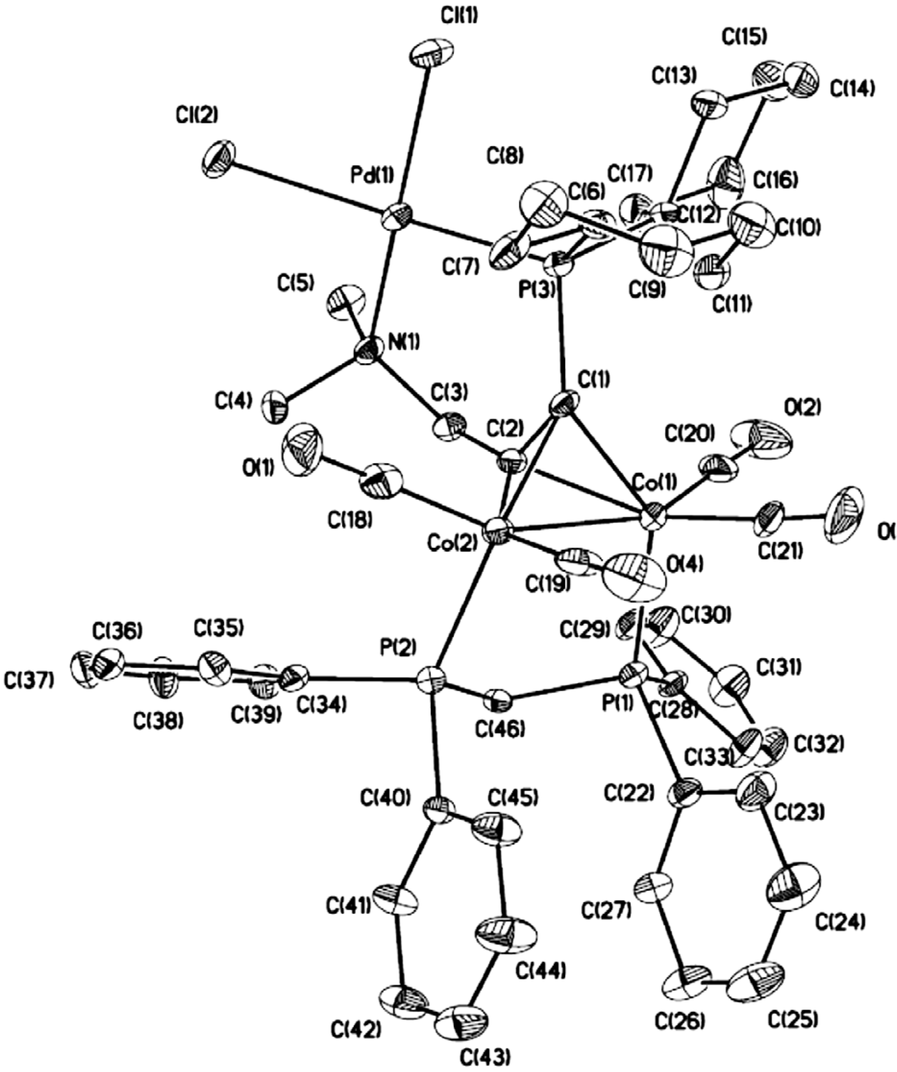


Fig. 1. ORTEP drawing of **5c**. Hydrogen atoms are omitted for clarity.

2.2. Structural comparison of *5c* and *7a*

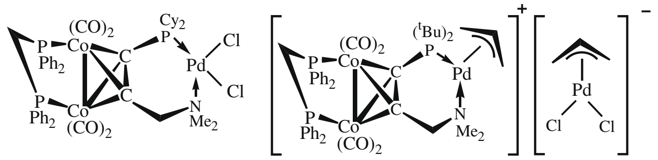
The structures of **5c** and **7a** reveal that each molecule is consisted of a P,N-ligands and palladium fragment (see Diagram 1). The structural comparison of **5c** and **7a** are listed in Table 2. As shown, the bond lengths of Pd–P and Pd–N are all shorter in **5c** than in **7a**. It is also true for the Pd–Cl bonds. The bond angle of P–Pd–N is narrower in **5c** than in **7a**. The bond angle of Cl–Pd–Cl is also much wider in **7a** than in **5c**.

Table 2
Comparison for selected structural parameters of **5c** and **7a**.

	5c	7a
Bond length(Å)		
Pd–P	2.241(2)	2.3227(14)
Pd–N	2.180(7)	2.226(4)
Pd–Cl(1)	2.296(2)	2.3856(16)
Pd–Cl(2)	2.425(2)	2.3693(18)
Bond angle(°)		
P–Pd–N	97.51(18)	100.03(11)
Cl–Pd–Cl	88.49(9)	97.61(6)

2.3. Application of *4c* in palladium-catalyzed amination reactions

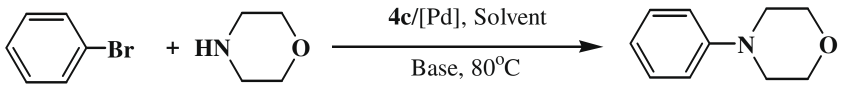
As known, an efficient metal-catalyzed cross-coupling reaction is regulated by a number of factors such as palladium salt, ligand, base, solvent, temperature and reaction hour [2]. Here, the general procedures for the optimization on the reaction conditions for the amination process was surveyed as the follows (Scheme 2). A proper sized Schlenk tube was charged with a magnetic stirrer then was placed with 1.0 mmol of bromobenzene, 1.2 equiv. of morpholine, 1.4 equiv. of base, 1.0 mL of solvent, and 1.0 mmol% of **4c**/palladium salt. The mixture was stirred while heating for certain time and then workup followed.



5c **7a**

Diagram 1. Generalized structure for **5c** and **7a**.

According to the generally accepted mechanism, deprotonation of the coordinated amine is one of the most critical steps in the catalytic cycle of amination reaction. Thereby, a well-chosen base is



Scheme 2.

essential to the performance of a catalytic reaction. As shown in Table 3, a rather good yield (>91%) was obtained when the reaction temperature was raised up from 60 to 80 °C (Entry 2). At the elevated temperature, the best base/solvent combination is NaO^{t}Bu/toluene. Other bases did not show encouraging results. The good performance of this combination might partly be due to the reducing capability of NaO^{t}Bu in toluene solvent.

The catalytic performance of a coupling reaction is also greatly affected by the particular palladium salt employed. Two factors are among the most concerned. First, the reduction potentials of Pd(II) to Pd(0) shall be different for various palladium sources used; second, the solubility of the potential intermediate(s) shall be different for various combinations of ligand/palladium salt. As shown, an excellent yield was obtained with either Pd(COD)Cl_2 or [(η^3-C_3H_5)PdCl]$_2$ as palladium source (Table 4, Entries 2 and 4). Although the latter complex is very efficient, the use of this complex is not practical due to its sensitivity to air. Unexpectedly, the commonly used Pd(OAc)$_2$ did not show competitive result in this case (Entry 1). As reported in a palladium free study, CuI alone plays a major role as the catalyst precursor in the coupling reaction [64]. It had been tested. Nevertheless, no observable reactivity had been shown here (Entry 7).

To establish the best ligand-to-metal ratio, the amination reaction was carried out under various **4c**/[(η^3-C_3H_5)PdCl]$_2$ molar ratios and conditions shown in Table 5. The best yield was achieved with 1:0.5 ratio (Table 5, Entry 3). This observation is worth noting since it is generally believed that two molar equiv. of a monodentate phosphine ligand are required for an effective catalytic Suzuki reaction [65]. Moreover, it is consistent with the molecular structure of **5c**. Ligand **4c** here acts as a bidentate ligand. Nevertheless, it seems that the active catalytic species in the amination reactions are different for using **4a** or **4c** as ligand.

Subsequently, the impact of various solvents on the reaction was evaluated. As demonstrated, the reaction rate is greatly affected by the solvent used (Table 6). For instance, the coupling reactions in 1,4-dioxane, THF and DMF are ineffective (Entries 2–4). However, the yield was greatly improved when toluene was used as a solvent (Entry 1). Extensive application of eco-friendly solvents such as water in chemical reaction is a touching appeal of Green Chemistry [66,67]. Nevertheless, the reaction employed water as the solvent turned out to be rather ineffective probably due to its insolubility of catalyst in water (Entry 5). A mixed solvent system, however, did show better result (Entry 6).

Interestingly, the efficiency of the coupling reaction is affected by the amount of solvent used (Table 7). The best efficiency was observed while more concentrated solution was present (Entry 1).

Table 3
Amination reaction using **4c**/[(η^3-C_3H_5)PdCl]$_2$ and various bases.[a]

Entry	Base	Temperature (°C)	NMR conversion (%)[b]
1	NaO^{t}Bu	60	22.4
2	NaO^{t}Bu	80	91.4
3	KF	80	Trace
4	K_2CO_3	80	Trace
5	K_3PO_4	80	Trace
6	NaOH	80	Trace

[a] Reaction conditions: 1.0 mmol of bromobenzene, 1.2 mmol morpholine, and 1.4 mmol of base, 2.0 mL toluene, 1.0 mmol% **4c**/[(η^3-C_3H_5)PdCl]$_2$, 2 h.
[b] Average of two runs.

Table 4
Amination reaction using various Pd sources.[a]

Entry	Pd source	NMR conversion (%)[b]
1	Pd(OAc)$_2$	34.9
2	Pd(COD)Cl_2	67.4
3	$PdCl_2(CH_3CN)_2$	2.2
4	[(η^3-C_3H_5)PdCl]$_2$	91.4
5	$Pd_2(dba)_2$	27.8
6	Pd(acac)$_2$	30.9
7	CuI/4c	N.R.
8	**5c**	78.0
9	**7c**	95.3
10	**7cB**	85.5

[a] Reaction conditions: 1.0 mmol of bromobenzene, 1.2 mmol morpholine, and 1.4 mmol of NaO^{t}Bu, 2.0 mL toluene, **4c**/[Pd] = 1:1, 80 °C, 2 h.
[b] Average of two runs.

Table 5
Amination reaction under various **4c**/[(η^3-C_3H_5)PdCl]$_2$ ratios.[a]

Entry	**4c**/[(η^3-C_3H_5)PdCl]$_2$ (mmol%)	**4c**/Pd atom (mmol%)	NMR conversion (%)[b,c]
1	0:0.5	0:1	3.0 (trace)
2	0.5:0.5	0.5:1	27.8 (14.6)
3	1:0.5	1:1	91.4 (83.1)
4	2:0.5	2:1	72.3 (52.6)
5	1:0.25	1:0.5	26.1 (12.7)
6	1:1	1:2	40.5 (97.9)

[a] Reaction conditions: 1.0 mmol of bromobenzene, 1.2 mmol morpholine, and 1.4 mmol of NaO^{t}Bu, 2.0 mL toluene, various ratios of **4c**/[(η^3-C_3H_5)PdCl]$_2$, 80 °C, 2 h.
[b] Average of two runs.
[c] Values in parentheses are taken from Ref. [49]. Amination reactions were carried out with **4a**/[(η^3-C_3H_5)PdCl]$_2$ as catalytic precursor.

Table 6
Amination reaction employing **4c**/[(η^3-C_3H_5)PdCl]$_2$ in various solvents.[a]

Entry	Solvent	NMR conversion (%)[b]
1	Toluene	91.4
2	1,4-Dioxane	16.3
3	THF	3.8
4	DMF	N.R.
5	H_2O	1.2
6	MeOH/H_2O (1:1)	42.8

[a] Reaction conditions are the same as in the footnote of Table 5 except for the solvent used.
[b] Average of two runs.

Table 7
Dependence of the yield of the amination reaction in amount of solvent used.[a]

Entry	Toluene (mL)	NMR conversion (%)[b]
1	1.0	>99.0
2	2.0	91.4
3	3.0	82.0

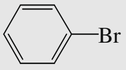
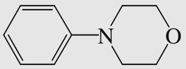
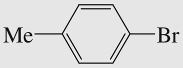
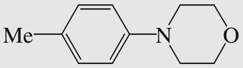
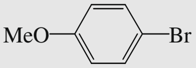
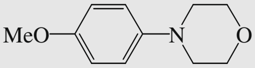
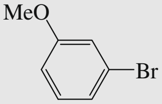
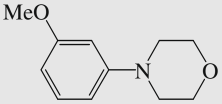
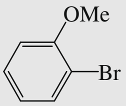
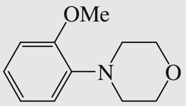
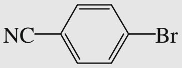
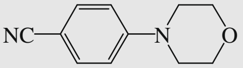
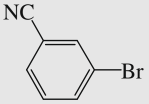
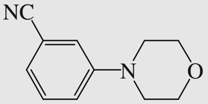
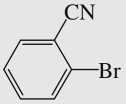
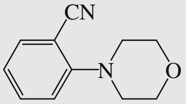
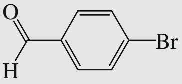
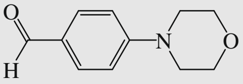
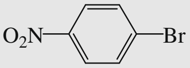
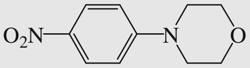
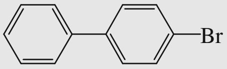
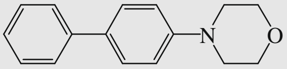
[a] Reaction conditions are the same as in the footnote of Table 5 except for the amount of toluene used.
[b] Average of two runs.

It is a common observation that better conversion is achieved with aryl halides bearing an electron-withdrawing rather than an electron-donating substituent in a palladium-catalyzed Suzuki coupling reaction [16]. Indeed, it is basically correct for the reaction with the oxidative addition process as the rate-determining-step (r.d.s.). Nevertheless, it may not be true for other reactions, such as Heck reaction, where the r.d.s. might be anywhere but the oxidative addition process [68,69,63,70]. As shown in Table 8, excellent performance was observed for substances with electron-withdrawing group (Entries 9–11). Poor performances were observed for substances with electron-donating group (Entries 2 and 3). It is consistent with the common observation. The unacceptable performances of the cyano-substituted bromobenzene might be caused by the coordination of the cyano-substituent to the palladium center thus to retard the activity of the catalyst (Entries 6–8).

For comparison, results from the same amination reaction with similar conditions for using **4a** as active ligand (Ref. [49]) were added to Table 8. In general, **4a** is a more efficient ligand than that of **4c**. It confirms the general observation that the efficiencies of the trialkylphosphines bearing bulky substituent are in the order of –^{t}Bu > –Cy. It seems that the factor of the reductive elimination process dominates the final reaction rate.

After the extensive survey of the **4c** assisted palladium complex catalyzed amination reaction, the optimized condition was found to be carried out in toluene at 80 °C with NaO^{t}Bu as base and [(η^3-C_3H_5)PdCl]$_2$ as the palladium salt. Nevertheless, this result is inferior to Buchwald's work on similar system which stated an

Table 8
Dependence of the yield of the amination reaction using **4c**/[(η^3-C_3H_5)PdCl]$_2$ on substrate.[a]

Entry	Substrate	Product	Yield (%)[b]
1			>99.0 (98.0)
2			67.6 (93.5)
3			58.4 (94.0)
4			17.4 (87.2)
5			Trace (14.5)
6			12.2 (NA)
7			26.6 (54.0)
8			4.3 (NA)
9			>99.0 (98.0[c])
10			88.9 (NA)
11			>99.0 (NA)

[a] Reaction conditions: 1.0 mmol of aryl halide, 1.2 mmol morpholine, and 1.4 mmol of NaO^{t}Bu, 1.0 mL toluene, 1 mol% **4c**/[(η^3-C_3H_5)PdCl]$_2$, 80 °C, 2 h, isolated yields, average of two runs.

[b] Values in parentheses are taken from Ref. [49]. Amination reactions were carried out with **4a**/[(η^3-C_3H_5)PdCl]$_2$ as catalytic precursor.

[c] 0.5 h.

excellent performance on amination of arylcholide and morpholine in mild condition by using Davephos (2-dicylohexylphosphino-2-N,N-dimethylamnobiphenyl) as the active P,N-ligand [71].

2.4. Applications of **4c** in palladium-catalyzed Suzuki reactions

The optimized condition for employing **4c**/palladium salt in Suzuki reaction was surveyed by varying factors, such as the sources of palladium salt, base, solvent, temperature, and reaction hour. The general procedures for the Suzuki coupling reaction were shown as the follows. The reaction was proceed with 1.0 mmol 4-bromobenoaldehyde, 1.2 mmol phenylboronic acid, 2.0 mmol base in 1.0 mL solvent, and with 1.0 mol% of **4c**/palladium salt, under designated temperature and reaction times depending on the reactions executed.

To begin with, the efficiencies of the reactions with various palladium salts were examined. Reactions were carried out using **4c** as a ligand in K_3PO_4/toluene system (Table 9). The ratio of ligand to number of palladium atom is 1:1. Reactions were carried out under 85 °C for one hour. Excellent performances were observed for using $Pd(OAc)_2$, $Pd_2(dba)_3$ and $Pd(acac)_2$ as the palladium sources (Entries 1–3). In order to differentiate the efficiencies of these three palladium salts, the reaction temperature was lowered to 55 °C and the solution was stirred for 1.5 h. $Pd(OAc)_2$ was found as a better palladium source in this case (Entries 7–9).

Compound **4c** is a potential bidentate ligand. In principle, it shall be able to bind to palladium atom in a chelating mode. Suzuki reactions were carried out in toluene in the presence of K_3PO_4 under various **4c**/$Pd(OAc)_2$ ratios in order to determine the preferred coordinating manner (Table 10). As expected, the optimum yield was achieved with **4c**/$Pd(OAc)_2$ = 1/1 (Entry 1). It indicates that **4c** most likely acts as a bidentate ligand and the conformation of the active species in this reaction might be similar as **5c**.

As known, the kind of base employed in Suzuki reaction is crucial to the catalytic efficiency [72–74]. The influence of the base used in this reaction was examined (Table 11). As shown, the best performance was observed with K_3PO_4 (Entry 4). Unexpectedly, the yield was noticeably low when a strong base such as NaO^{t}Bu was employed (Entry 1). No conversion of the reactants was observed in the absence of base (Entry 6).

Table 9
Dependence of the Suzuki reaction yield on the Pd sources.[a]

Entry	Pd source	Time (h)	Temperature (°C)	Conversion (%)[b]
1	$Pd(OAc)_2$	1.0	85	>99.0
2	$Pd_2(dba)_3$	1.0	85	>99.0
3	$Pd(acac)_2$	1.0	85	>99.0
4	$[(\eta^3\text{-}C_3H_5)PdCl]_2$	1.0	85	54.9
5	$Pd(COD)Cl_2$	1.0	85	27.2
6	$PdCl_2(CH_3CN)_2$	1.0	85	47.2
7	$Pd(OAc)_2$	1.5	55	42.9
8	$Pd_2(dba)_3$	1.5	55	37.9
9	$Pd(acac)_2$	1.5	55	26.2

[a] Reaction conditions: 1.0 mmol of aryl halide, 1.2 mmol phenylboronic acid, and 2.0 mmol of K_3PO_4, 2.0 mL toluene, 1 mmol% **4c**/[Pd], determined by NMR.
[b] Average of two runs.

Table 10
Dependence of the Suzuki reaction yield on the **4c**/$Pd(OAc)_2$ ratio.[a]

Entry	**4c**/$Pd(OAc)_2$ (mmol%)	Conversion (%)[b]
1	1:1	>99.0
2	2:1	54.7
3	1:0.5	43.4
4	1:2	28.3
5	0.5:0.5	19.7
6	1:0	Trace

[a] Reaction conditions: 1.0 mmol of aryl halide, 1.2 mmol phenylboronic acid, and 2.0 mmol of K_3PO_4, 2.0 mL toluene, 85 °C, 1 h, 1 mmol% **4c**/$Pd(OAc)_2$.
[b] Average of two runs, determined by NMR.

Table 11
Suzuki reactions employing **4c**/$[(\eta^3\text{-}C_3H_5)PdCl]_2$ and various bases.[a]

Entry	Base	Yield (%)[b]
1	NaO^{t}Bu	53.4
2	KF	24.4
3	K_2CO_3	71.0
4	K_3PO_4	>99.0
5	NaOH	91.3
6	-	N.R.

[a] Reaction conditions: 1.0 mmol of aryl halide, 1.2 mmol phenylboronic acid, and 2.0 mmol of base, 2.0 mL toluene, 85 °C, 1 h, 1 mmol% **4c**/$Pd(OAc)_2$.
[b] Average of two runs, determined by NMR.

Table 12
Dependence of the Suzuki reaction yield on solvent.[a]

Entry	Solvent	Conversion (%)[b]
1	Toluene (1 mL)	>99.0
2	Toluene (2 mL)	>99.0
3	Toluene (3 mL)	67.6
4	1,4-Dioxane	84.0
5	H_2O	Trace
6	DMF	67.2

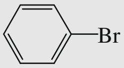
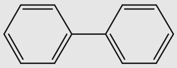
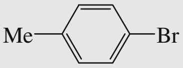
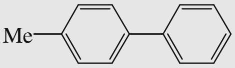
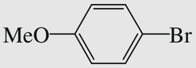
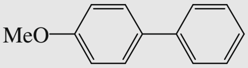
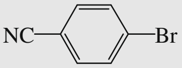
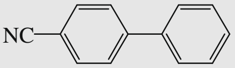
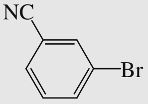
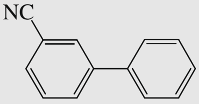
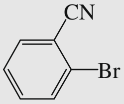
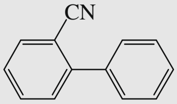
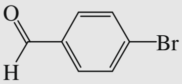
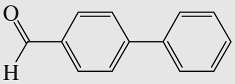
[a] Reaction conditions: 1.0 mmol of aryl halide, 1.2 mmol phenylboronic acid, and 2.0 mmol of K_3PO_4, 2.0 mL solvent, 85 °C, 1 h, 1 mmol% **4c**/$Pd(OAc)_2$.
[b] Average of two runs, determined by NMR.

The solubility of the reactants and catalyst in the solvent is critical to the success of the coupling reaction. The concentration of the reaction is also crucial. Subsequently, the impacts of various solvents on the reactions were evaluated. As shown in Table 12, the reaction is greatly affected by the nature of the solvent used. For instance, the coupling reactions in toluene and 1,4-dioxane were rather effective (Entries 1–4). However, the performance was not acceptable for the rest of solvents. Although water is regarded as a solvent of ecological friendly, the insolubility of reactants and catalyst in aqueous solution limits it application. The effect of the concentration of the reaction is also demonstrated. The efficiency is better for more concentrated solution (Entry 1).

As mentioned, a better conversion is achieved with aryl halides bearing an electron-withdrawing rather than an electron-donating substituent in a palladium-catalyzed Suzuki coupling reaction [16]. As shown in Table 13, less efficient performances were observed for the substances with electron-donating groups (Entries 2 and 3). On the contrast, the catalytic performance was excellent for the substance with electron-withdrawing group (Entry 7). Nevertheless, the performances were not as expected for substance with electron-donating group –CN (Entries 4–6). Beside the severe steric effect plays in Entry 6, the unacceptable performances of the cyano-substituted bromobenzene might be caused by the coordination of cyano- to palladium center thus to retard the activity of the catalyst (Entries 4 and 5).

For comparison, Suzuki reactions as shown in Scheme 3 were carried out in toluene employing a P,N-ligand **4c**-chelated $Pd(OAc)_2$ or a P,P-ligand chelated palladium complex **8** [75]. A satisfying conversion rate, 91.7%, was observed using **4c**/$Pd(OAc)_2$ as the catalyst precursor when the reaction was carried out at 65 °C for 5 h; it was only 71.6% conversion for **8** while carried out under the same temperature for 16 h. Obviously, the performance of the palladium complex with the P,N-ligand surpasses that with the P,P-ligand in this reaction condition (see Diagram 2).

Table 13
Dependence of the yield of the Suzuki reaction using **4c**/$Pd(OAc)_2$ on substrate.[a]

Entry	Substrate	Product	Conversion (%)[a]
1			>99.0
2			55.0
3			42.1
4			78.7
5			80.2
6			65.2
7			>99.0[b]

[a] Reaction conditions: 1.0 mmol of arylhalide, 1.2 mmol phenylboric acid, and 2.0 mmol of K_3PO_4, 2.0 mL toluene, 1.0 mmol% **4c**/$Pd(OAc)_2$, 85 °C, 2 h, isolated yields, average of two runs.

[b] 1 h.

2.5. Summary

We have developed a general route for the preparation of several fascinating cobalt-containing P,N-bidentate ligands. These ligands have proven to be fairly efficient in the palladium-catalyzed aryl halide amination reaction. A P,N-chelated palladium complex **5c** was characterized by spectroscopic means as well as single-crystal X-ray diffraction method. Fair to excellent performances of **4c**/palladium salt *in situ* or isolated **5c** in amination as well as Suzuki reactions were resulted in designated reaction conditions. This work also confirms the general observation that the efficiencies of the trialkyl- or triaryl-phosphines bearing bulky substituent are in the order of $-{}^t$Bu > $-$Cy > $-$Ph.

3. Experimental

3.1. General

All operations were performed in a nitrogen flushed glove box or in a vacuum system. Freshly distilled solvents were used. All processes of separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924) or column chromatography. GC analyses were performed on a HP-5890 FID GC with a QUADREX 007-CW fused silica 30 m column, and data were recorded on a HP ChemStation. Most of the ^{1}H NMR spectra were recorded on a 300 MHz Varian VXR-300S spectrometer. In addition, some routine ^{1}H NMR spectra were recorded either on a Gemini-200 spectrometer at 200.00 MHz or Varian-400 spectrometer at 400.00 MHz. The chemical shifts are reported in ppm relative to internal standards $CHCl_3$ (δ 7.26), CH_2Cl_2 (δ 5.30) or $CH_3C({=}O)CH_3$ (δ 2.09). ^{31}P and ^{13}C NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. The chemical shifts for the former and the latter are reported in ppm relative to internal standards H_3PO_4 (δ 0.0) and $CHCl_3$ (δ 77) or CH_2Cl_2 (δ 53), respectively. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were recorded on Heraeus CHN-O-S-Rapid.

3.2. Synthesis and characterization of **5c**

A 100 mL round-bottom flask equipped with a magnetic stirrer was charged with 1.00 mmol of **4c** (0.894 g), one molar equiv. of $Pd(COD)Cl_2$ (1.00 mmol, 0.286 g) and 15 mL toluene. The solution was stirred at 25 °C for 10 min before the solvent was removed under reduced pressure. The residue was dissolved in 5 mL CH_2Cl_2 and then further separated by CTLC. A yellowish-brown band was eluted out by ethyl acetate and was identified as $(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4(\mu,\eta\text{-}Cy_2PC{\equiv}CCH_2NMe_2)PdCl_2$ **5c**. The yield was 91.3% (0.913 mmol, 0.978 g).

3.2.1. Selected spectroscopic data for **5c**

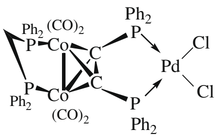
^{1}H NMR(CD_2Cl_2, δ (ppm)): 7.68–7.15 (m, 20H, arene), 3.70 (q, 2H, dppm), 3.41 (s, 2H, CH_2), 2.35–2.10 (m, 6H, CH_3), 2.07–1.25 (m, 22H, cyclohexyl); ^{31}P NMR($CDCl_3$, δ (ppm)): 49.3 (s, 1P, $P(Cy)_2$), 38.8 (s, 2P, dppm); ^{13}C NMR (CD_2Cl_2, δ (ppm)): 206.0–202.2 (s, 4C, CO), 137.1–128.8 (m, 24C, arene), 107.5 (s, 1C, P–C≡**C**), 67.2 (s, 1C, C–N), 50.7 (s, 6C, N–C) 38.6 (t, 1C, dppm), 28.3–26.2 (m, 12C, cyclohexyl); MS (FAB): *m/z* = 1016 $[M-2CO]^+$; Anal. Calc.: C, 51.59; H, 4.89; N, 1.31. Found: C, 48.56; H, 5.78; N, 0.93%.

3.3. Synthesis and characterization of **7c**

A 100 mL round-bottom flask equipped with a magnetic stirrer was charged with 0.01 mmol of **4c** (0.0089 g), one molar equiv. of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.01 mmol, 0.0036 g) and 5 mL toluene. The solution was stirred at 25 °C for 30 min before the solvent was removed under reduced pressure. The residue was dissolved in 5 mL CH_2Cl_2 and then further separated by CTLC. A dark-red band was eluted out by ethyl acetate and was identified as $[(\mu\text{-}PPh_2CH_2PPh_2)\text{-}Co_2(CO)_4(\mu,\eta\text{-}Cy_2PC{\equiv}CCH_2NMe_2)Pd(\eta^3\text{-}C_3H_5)]^+ [(\eta^3\text{-}C_3H_5)PdCl_2]^-$ (**7c**). The yield was 99% (0.0099 mmol, 0.011 g).

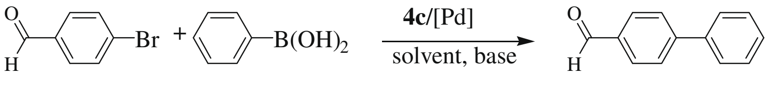
3.3.1. Selected spectroscopic data for **7c**

^{1}H NMR(CD_2Cl_2, δ (ppm)): 7.46–7.12 (m, 20H, arene), 5.59, 4.49 (m, 2H, allylic HHC=C(**H**)–CHH), 4.01 (d, J_{H-H} = 6.8 Hz, 4H, allylic



8

Diagram 2.



Scheme 3.

H**H**C═C(H)–C**H**H), 2.96 (d, $J_{H–H}$ = 12.4 Hz, 4H, allylic **H**HC═C(H)–CH**H**), 3.72 (m, 2H, dppm), 3.58 (s, 2H, –C**H**$_2$N(CH$_3$)$_2$), 2.29 (s, 6H, –CH$_2$N(C**H**$_3$)$_2$), 2.05–1.34 (m, 22H, cyclohexyl); ^{31}P NMR(CDCl$_3$, δ (ppm)): 47.4 (s, 1P, P(Cy)$_2$), 39.7 (s, 2P, dppm); ^{13}C NMR (CD$_2$Cl$_2$, δ (ppm)): Cation: 206.5–202.8 (s, 4C, CO), 137.6–128.7 (m, 24C, arene), 120.2 (s, 1C, allylic C═**C**–C), 106.8 (s, 1C, P–C≡**C**), 70.8 (d, 1C, P–**C**≡C), 66.8 (s, 1C, C–N), 62.2 (m, 2C, allylic **C**═C–**C**), 45.0 (s, 6C, N–C), 37.6 (t, 1C, dppm), 30.7 (s, 4C, (Cy)$_2$), 29.2 (s, 4C, (Cy)$_2$), 27.5, 27.0 (d, $J_{C–P}$ = 25.6 Hz, $J_{C–P}$ = 53.1 Hz, 2C, P(Cy)$_2$), 26.2 (s, 4C, (Cy)$_2$); Anion: 110.8 (s, 1C, allylic C═**C**–C), 55.4 (2C, allylic **C**═C–**C**); MS (FAB): *m/z* = 1042 [M]$^+$.

3.4. Synthesis and characterization of ***7cB***

A 100 mL round-bottom flask equipped with a magnetic stirrer was charged with 0.01 mmol of **4c** (0.0089 g), 0.005 mmol of [(η^3-C$_3$H$_5$)PdCl]$_2$ (0.0018 g), 0.005 mmol of NaBF$_4$ (0.0006 g) and 5 mL toluene. The solution was stirred at 25 °C for 30 min before the solvent was removed under reduced pressure. The orange-red colored residue was purified by CTLC and was identified as [(μ-PPh$_2$CH$_2$-PPh$_2$)Co$_2$(CO)$_4$(μ,η-Me$_2$NCH$_2$C≡CP(Cy)$_2$)Pd(η^3-C$_3$H$_5$)]$^+$[BF$_4$]$^-$ (**7cB**). The yield was 99%.

3.4.1. Selected spectroscopic data for ***7cB***

^{1}H NMR(CD$_2$Cl$_2$, δ (ppm)): 7.43–7.10 (m, 20H, arene), 5.48 (m, 1 H, allylic HHC═C(**H**)–CHH), 4.47 (m, 1H, dppm) 4.07 (d, 2H $J_{H–H}$ = 6.8 Hz, 2H, allylic H**H**C═C(H)–C**H**H), 3.36 (m, 1H, dppm), 3.01 (d, $J_{H–H}$ = 12.0 Hz, 2H, allylic **H**HC═C(H)–CH**H**), 2.64 (s, 2H, –C**H**$_2$N(CH$_3$)$_2$), 1.92 (s, 6H, –CH$_2$N(C**H**$_3$)$_2$), 2.07–1.26 (m, 22 H, cyclohexyl);

^{13}C NMR (CD$_2$Cl$_2$, δ (ppm)): 206.5–202.7 (s, 4C, CO), 137.6–128.5 (m, 24C, arene), 120.2 (s, 1C, allylic C═**C**–C), 106.8 (s, 1C, P–C≡**C**), 86.6 (d, 1C, P–**C**≡C), 65.9 (s, 1C, C–N), 63.0 (m, 2C, allylic **C**═C–**C**), 44.9 (s, 6C, N–C), 37.0 (t, 1C, dppm), 31.3–26.2 (m, 12C, cyclohexyl);

MS (FAB): *m/z* = 1042 [M]$^+$; Anal. Calc.: C, 46.60; H, 5.04; N, 0.95. Found: C, 52.17; H, 5.09; N, 1.24%.

3.5. General procedure for amination reactions

An oven-dried Schlenk tube was charged with **4c** (0.01 mmol, 0.0089 g), [(η^3-C$_3$H$_5$)PdCl]$_2$ (0.005 mmol, 0.0018 g) and a base (1.4 mmol). The tube was evacuated and backfilled with nitrogen followed by the addition of an aryl bromide (1.00 mmol), toluene (1.0 mL) and morpholine (1.20 mmol). The tube was sealed with a Teflon screw cap, and the mixture was stirred at 80 °C for 2 h. After all starting materials had been consumed; the mixture was allowed to cool down to room temperature and then diluted with ether (40 mL). The resulting suspension was transferred into a separatory funnel and washed with water (10 mL). The organic layer was separated, dried with anhydrous MgSO$_4$ and concentrated under reduced pressure. The crude residue was purified by CTLC with hexane/ethyl acetate as a mobile phase. The solvent was removed under reduced pressure, and the yield of the eluted product was determined.

3.6. X-ray crystallographic studies

Suitable crystals of **5c** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package [76]. All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms [77]. Crystallographic data for compounds **5c** are summarized in Table 1.

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Appendix A. Supplementary material

CCDC 692831 contains the supplementary crystallographic data for compound **5c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.046.

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