Journal of Organometallic Chemistry 694 (2009) 2555–2561

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Facile synthesis of achiral and chiral PCN pincer palladium(II) complexes and their application in the Suzuki and copper-free Sonogashira cross-coupling reactions

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ARTICLE INFO

Article history:
Received 25 November 2008
Received in revised form 31 March 2009
Accepted 3 April 2009
Available online 16 April 2009

Keywords:
PCN pincer palladium(II) complexes
Phosphinite
Aldimine
Chiral
Suzuki reaction
Sonogashira reaction

ABSTRACT

Five non-symmetrical PCN pincer palladium(II) complexes [PdCl{C_6H_3-2-(CH=NR)-6-(OPR'_2)}] (R = *m*-ClC_6H_4, R′ = Ph (**2a**); R = Ph, R′ = Ph (**2b**); R = *i*-Pr, R′ = Ph (**2c**); R = *m*-ClC_6H_4, R′ = *i*-Pr (**2d**); R = (*S*)-1-phenylethyl, R′ = Ph (**2e**)) have been easily prepared in only two steps from readily available *m*-hydroxybenzaldehyde and characterized by HRMS, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and IR spectra. The molecular structures of **2a** and **2b** have been further determined by X-ray single-crystal diffraction. The obtained Pd complexes were found to be effective catalysts for the Suzuki and copper-free Sonogashira cross-coupling reactions which could be carried out in the undried solvent under air.

1. Introduction

Ever since Molton and Shaw first reported PCP type metal pincer complexes (the term PCP refers to the three atoms directly attached to the metal) based on the diphosphine ligands 1,3-$(R_2PCH_2)_2C_6H_4$ in the 1970s [1], this class of complexes have played important roles in not only both homogeneous and heterogeneous catalysis in organic synthesis but also in the materials science [2–9]. Among them, the most common pincer palladacycles are YCY types (Y = NR_2, PR_2, OPR_2, SR, etc.), which are symmetrical with two identical donor groups and two equivalent five-membered metallacycles. Due to the existence of the Pd–C σ bonds supported by two *ortho*,*ortho*-chelated heteroatom groups in the molecules, these complexes usually exhibit high stabilities towards heat, air and moisture. Furthermore, the reactivity of the Pd center can be finely tuned by adjusting the steric and electronic properties of heteroatom donors and substituents thereon [10–20]. Consequently, various types of PCP or NCN pincer palladium complexes have been found to be efficient catalysts for a variety of C–C bond forming reactions including the Heck reaction [10,13,14,21], Suzuki coupling [16,22,23], Sonogashira coupling [15] and α-arylation of ketones [24]. Taking these results into account, it seems very interesting to develop hybrid, non-symmetrical YCY′ pincer Pd complexes such as PCN type since different donors ("hard" N and "soft" P in PCN pincers) may provide a better tuning of the catalytic properties or give unique reactivity. By contrast, the synthesis and applications of non-symmetrical pincer Pd complexes have less often been reported [25–30]. This is partly because their preparation is a considerable challenge, which is laborious and requires a series of steps to introduce different donors. Recently, we developed a facile, direct method based on one-pot phosphorylation/palladation reaction for the preparation of non-symmetrical PCN pincer palladium complexes containing phosphinito group [31]. These compounds were conveniently synthesized by the reaction of pyrazolyl or amino-containing *m*-phenol derivatives with dialkylchorophosphine in the presence of triethylamine in refluxing toluene, followed by the addition of palladium chloride (Scheme 1). This one-pot phosphorylation/palladation strategy avoided the usually troublesome step of isolating the air- and moisture-sensitive phosphinite ligands. Another feature of the method is that C2 palladation can be accomplished via direct C_{aryl}–H activation of the related 1,3-disubstituted benzene during the reaction by using cheap and commercially available palladium chloride. Therefore, it is unnecessary to prepare appropriate 1,2,3-trisubstituted benzene (in the oxidative addition and transmetalation method) and the synthetic procedures were thus simplified. To further extend this one-pot synthetic strategy, herein we report a series of new PCN pincer palladium complexes **2a–e** that feature a phenyl backbone, a phosphinito group, and an aldimino group (Scheme 2). Among them, **2e** is a kind of chiral PCN pincer complex. To our knowledge, only Motoyama et al. described chiral

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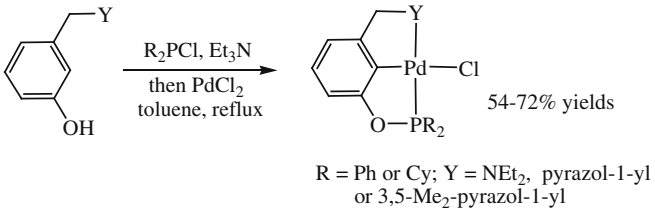
doi:10.1016/j.jorganchem.2009.04.002



Scheme 1. One-pot phosphorylation/palladation reaction for the synthesis of the PCN pincer palladium complexes.

versions of PCN pincer palladium complexes with (oxazolinyl)phenyl phosphinite ligands via oxidative addition of an appropriate bromo-substituted derivative [32]. In connection with our own experience in the Pd-catalyzed reactions for the formation of C–C or C–N bonds [33–37], the obtained Pd compounds were applied to Suzuki and copper-free Sonogashira cross-coupling reactions. The results are shown as below.

2. Results and discussion

2.1. Synthesis and characterization

The achiral and chiral PCN pincer complexes **2a–e** were readily prepared in only two steps from commercially available starting materials as shown in Scheme 2. First, condensation of *m*-hydroxybenzaldehyde with achiral amine or chiral (*S*)-1-phenylethylamine in the presence of activated Al_2O_3 in toluene at reflux proceeded smoothly to afford the corresponding *m*-hydroxybenzaldimines **1a–d**. The second step is one-pot phosphorylation/palladation reaction. Namely, **1a–d** reacted with diphenylchlorophosphine or diisopropylchlorophosphine in the presence of triethylamine in refluxing toluene for 1 h, followed by the addition of palladium chloride and refluxing for another 5 h. The new PCN pincer palladium complexes **2a–e** could be obtained in 45–48% isolated yields as pale yellow solids after chromatography on silica gel. All the pincer complexes are air- and moisture-stable both in the solid state and in solution. They were confirmed by HRMS, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and IR spectra.

The molecular structures of **2a** and **2b** were determined by X-ray single crystal analysis. The molecules are illustrated in Figs. 1 and 2, respectively. Selected bond lengths and bond angles are listed in Table 1. Crystal data are given in Table 2. The structural features of the two compounds are almost identical. The ligand in each complex is coordinated to the Pd(II) center via aldimine-N, phosphinite-P and the central aryl-C in a tridentate manner. The palladium atom adopts a typical distorted-square-planar configuration defined by C (central aryl), N, P and Cl atoms. All the bond distances and angles for the metal coordination sphere in **2a** and **2b** are similar. The Pd–C (around 1.96 Å) and Pd–P (around 2.20 Å) bond lengths are comparable to those in the related PCN

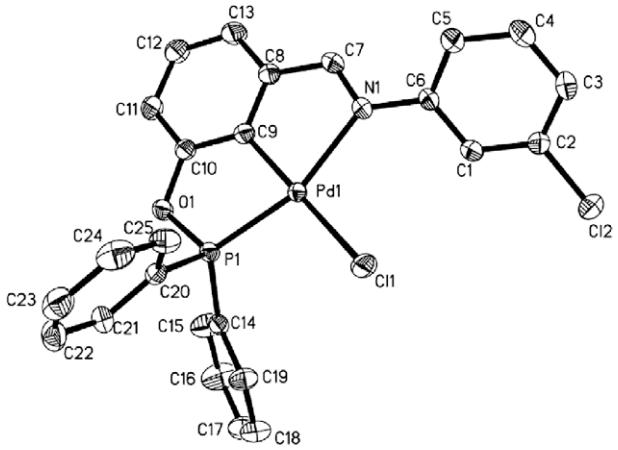


Fig. 1. Molecular structure of **2a**. Hydrogen atoms are omitted for clarity.

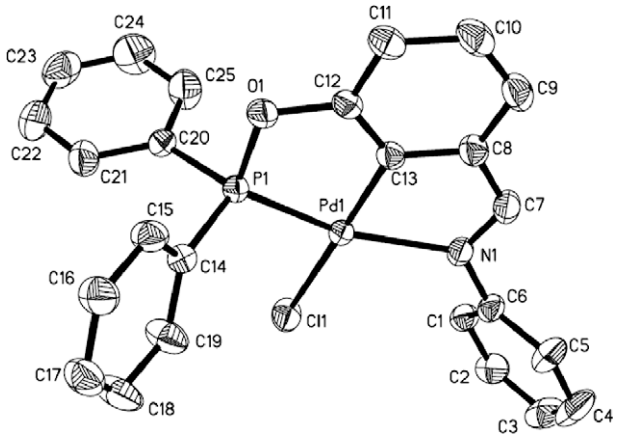
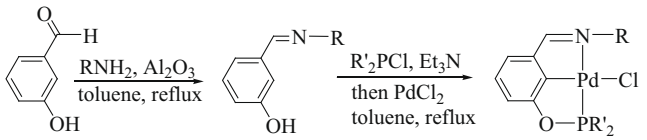


Fig. 2. Molecular structure of **2b**. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for PCN complexes **2a** and **2b**.

Complex	2a	2b
Pd(1)–C(9)/Pd(1)–C(13)	1.954(3)	1.963(3)
Pd(1)–N(1)	2.182(2)	2.175(2)
Pd(1)–P(1)	2.2033(8)	2.2006(9)
Pd(1)–Cl(1)	2.3637(8)	2.3674(10)
C(9)–Pd(1)–N(1)/C(13)–Pd(1)–N(1)	79.06(10)	78.84(12)
C(9)–Pd(1)–P(1)/C(13)–Pd(1)–P(1)	79.87(9)	79.93(10)
N(1)–Pd(1)–P(1)	158.93(6)	158.16(7)
C(9)–Pd(1)–Cl(1)/C(13)–Pd(1)–Cl(1)	176.66(8)	178.92(9)
N(1)–Pd(1)–Cl(1)	100.76(6)	101.47(8)
P(1)–Pd(1)–Cl(1)	100.26(3)	99.85(3)



1a R = *m*-ClC_6H_4
1b R = Ph
1c R = *i*-Pr
1d R = (*S*)-1-phenylethyl

2a R = *m*-ClC_6H_4; R' = Ph
2b R = Ph; R' = Ph
2c R = *i*-Pr; R' = Ph
2d R = *m*-ClC_6H_4; R' = *i*-Pr
2e R = (*S*)-1-phenylethyl; R' = Ph

Scheme 2. Synthesis of achiral and chiral PCN pincer Pd(II) complexes **2a–e**.

Table 2
Summary of crystal structure determination for PCN complexes **2a** and **2b**.

	2a	2b
Formula	$C_{25}H_{18}Cl_2NOPPd$	$C_{25}H_{19}ClNOPPd$
Molecular weight	556.67	522.23
Crystal size (mm)	0.20 × 0.18 × 0.17	0.20 × 0.18 × 0.17
a (Å)	27.173(5)	9.5883(19)
b (Å)	10.145(2)	13.689(3)
c (Å)	16.742(3)	17.565(4)
α (°)	90	90
β (°)	100.00(3)	105.78(3)
γ (°)	90	90
V (Å^3)	4545.2(16)	2218.6(8)
Z	8	4
Space group	$C2/c$	$P2(1)/c$
D_{calcd} (g cm^{-3})	1.627	1.564
μ (mm^{-1})	1.140	1.046
θ range (°)	1.52–25.50	1.91–25.50
Number of data collected	7400	7233
Number of unique data	4032	4063
R (all data)	0.0291	0.0355
R_w (all data)	0.0724	0.0868
F(0 0 0)	2224	1048

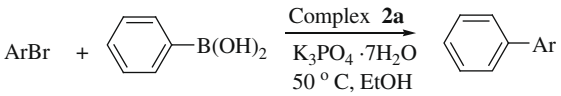
pincer palladium complex [30], but slightly shorter than those found in the symmetrical PCP-bis(phosphinite) pincer palladium complexes (1.97–2.02 and 2.26–2.29 Å, respectively) [21–23]. The Pd–N distances (around 2.18 Å) are longer than those NCN-bis(aldimine) pincer palladium complexes (2.054–2.126 Å) [13,38]. The angle of C–Pd–Cl (176.7° and 178.9°, respectively) is only slightly less than 180°, while the N–Pd–P angles (around 159°) are small, which are in accordance with a pincer consisting 2 five-membered-ring palladacycles [13,21–23,30] and reflects a relative steric strain of the almost planar tricyclic system.

2.2. Catalytic properties of Pd complexes

The effectiveness of PCN pincer Pd complexes **2** was first tested in the Suzuki reaction. Coupling of 4-bromotoluene with phenylboronic acid was chosen as a model to optimize the reaction conditions. The reaction was performed in the presence of 1 mol% of **2a** for 3 h under air in the undried solvent which was used as purchased. A quick survey of three bases in DMF at 110 °C revealed that $K_3PO_4 \cdot 7H_2O$ was more effective (Table 3, entries 1–3). Then the influence of several solvents were examined. Toluene and EtOH were found to be much better than others (entries 3–7). Further studies indicated that the reaction temperature could be lowered to 50 °C without loss of catalytic activity (entries 8–9). Thus, using 1 mol% of **2a** as the catalyst and $K_3PO_4 \cdot 7H_2O$ as the base in EtOH at 50 °C gave the coupled product 4-methylbiphenyl in almost quantitative yield after only 3 h (entry 9).

Under these reaction conditions, a variety of electronically and structurally diverse aryl bromides could be cross-coupled very efficiently with phenylboronic acid, affording the desired products in excellent yields. These aryl bromides included non-activated electron-neutral bromides such as bromotoluenes, 1-bromonaphthalene and bromobenzene, deactivated electron-rich 4-bromoanisole as well as bromopyridines (Table 4, entries 1–7). 2-Bromothiophene and the very sterically hindered 2-bromo-*m*-xylene could provide the corresponding biaryls in moderate yields (entries 8–9). Surprisingly, the activated electron-deficient 2-bromonitrobenzene only gave a low yield (entry 10). In the following

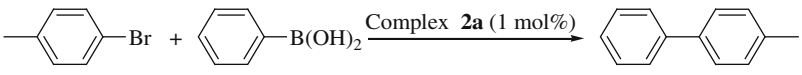
Table 4
Suzuki reactions of aryl bromides with phenylboronic acid catalyzed by PCN complex **2a**.



Entry	Catalyst (mol%)	Aryl bromide	Time (h)	Yield (%)[a]
1	**2a** (1)	3-Bromotoluene	3	>99
2	**2a** (1)	2-Bromotoluene	3	>99
3	**2a** (1)	1-Bromonaphthalene	3	95
4	**2a** (1)	Bromobenzene	3	>99
5	**2a** (1)	4-Bromoanisole	3	91
6	**2a** (1)	2-Bromopyridine	3	92
7	**2a** (1)	3-Bromopyridine	3	90
8	**2a** (1)	2-Bromothiophene	3	79
9	**2a** (1)	2-Bromo-*m*-xylene	3	78
10	**2a** (1)	2-Bromonitrobenzene	3	49
11	**2a** (0.5)	4-Bromotoluene	10	99
12	**2a** (0.3)	4-Bromotoluene	10	98
13	**2a** (0.2)	4-Bromotoluene	10	88
14	**2a** (0.1)	4-Bromotoluene	10	83
15	**2a** (0.3)	4-Bromoanisole	10	91
16	**2a** (0.1)	4-Bromoanisole	10	72
17	**2a** (0.3)	4-Bromonitrobenzene	10	>99
18	**2a** (0.3)	2-Bromonitrobenzene	10	87
19	**2a** (0.3)	2-Bromo-*m*-xylene	10	75
20	**2a** (0.3)	1-Bromonaphthalene	10	79
21	**2a** (0.3)	2-Bromopyridine	10	89
22	**2a** (0.3)	2-Bromothiophene	10	61

Reaction conditions: Aryl bromide (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), $K_3PO_4 \cdot 7H_2O$ (1.0 mmol), EtOH (3.0 mL), 50 °C, under air.
[a] Isolated yields.

Table 3
Optimization of reaction conditions for the coupling of 4-bromotoluene with phenylboronic acid.



Entry	Solvent	Base	Temperature (°C)	Yield (%)[a]
1	DMF	Na_2CO_3	110	30
2	DMF	K_2CO_3	110	64
3	DMF	$K_3PO_4 \cdot 7H_2O$	110	83
4	Dioxane	$K_3PO_4 \cdot 7H_2O$	110	80
5	DMF/H_2O (10:1)	$K_3PO_4 \cdot 7H_2O$	110	79
6	Toluene	$K_3PO_4 \cdot 7H_2O$	110	>99
7	EtOH	$K_3PO_4 \cdot 7H_2O$	Reflux	96
8	Toluene	$K_3PO_4 \cdot 7H_2O$	50	92
9	EtOH	$K_3PO_4 \cdot 7H_2O$	50	>99

Reaction conditions: Catalyst **2a** (1 mol %), 4-bromotoluene (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), base (1.0 mmol), solvent (3.0 mL), 3 h, under air.
[a] Isolated yields.

Table 5
Relative catalytic activities of PCN pincer Pd complexes **2a–e** and PCP Pd complex **3**.

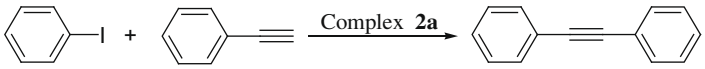
Entry	Catalyst (mol%)	Solvent	Aryl bromide	Time (h)	Yield (%)[a]
1	**2b** (0.3)	EtOH	4-Bromotoluene	10	98
2	**2b** (0.3)	EtOH	4-Bromoanisole	10	88
3	**2c** (0.3)	EtOH	4-Bromotoluene	10	95
4	**2c** (0.3)	EtOH	4-Bromoanisole	10	88
5	**2d** (0.3)	EtOH	4-Bromotoluene	10	82
6	**2e** (0.3)	EtOH	4-Bromotoluene	10	72
7	**2e** (0.3)	EtOH	4-Bromoanisole	10	70
8	**3** (0.3)	EtOH	4-Bromotoluene	10	89
9	**2a** (0.3)	Toluene	4-Bromotoluene	10	85
10	**3** (0.3)	Toluene	4-Bromotoluene	10	80
11	**3** (1)	Toluene	4-Bromotoluene	3	74

Reaction conditions: Aryl bromide (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), $K_3PO_4 \cdot 7H_2O$ (1.0 mmol), solvent (3.0 mL), 50 °C, under air.
[a] Isolated yields.

experiments, we found that reducing the catalyst loading to 0.3 mol% could still give excellent results by prolonging the reaction time to 10 h (entries 11–12). Further reduction in the amount of the catalyst led to a gradual decrease in the yields under the same reaction conditions (entries 13–14). By using 0.1–0.3 mol% of **2a**, coupling of several aryl bromides with $PhB(OH)_2$ could also afford the coupled products in good to excellent isolated yields (entries 15–22).

Finally, the relative catalytic activities of PCN pincer Pd complexes **2a–e** as well as the corresponding symmetrical PCP complex [$PdCl\{C_6H_3$-2,6-$(OPPh_2)_2\}$] (**3**) in the Suzuki reaction were investigated (Table 5). Compounds **2a**, **2b** and **2c** showed comparable activity in the coupling of 4-bromotoluene or 4-bromoanisole with phenylboronic acid and all the three complexes are more active than **2d**, **2e** and the symmetrical **3** under the same conditions (Table 4 entries 12, 15 vs. Table 5, entries 1–8). When the coupling was carried out in toluene, complex **2a** also exhibited higher activity than **3** giving 85% and 80% yields, respectively (Table 5, entries 9–10). And the difference of the activity between them was enlarged when using 1 mol% of the catalyst for 3 h in toluene (92% vs. 74% yield, Table 3, entry 8 vs. Table 5, entry 11). Due to the observation of palladium black formation during the reaction, we believed that the present Suzuki reactions should include a Pd(0)–Pd(II) catalytic cycle. To our knowledge, palladacycles including pincer palladacycles usually show high activities at 90–100 °C or higher temperatures for Pd-catalyzed C–C coupling reactions since high temperature helps the cleavage of stable palladacycles [Pd(II)] to form the catalytically active Pd(0) species [21–23]. For example, Dupont's PCN pincer complex was quite efficient for the Suzuki coupling of both deactivated and activated aryl chlorides with a catalyst loading of 1 mol% at 130 °C [39]. While the reaction of more reactive 4-bromoacetophenone with $PhB(OH)_2$ in the presence of 0.1 mol% of Uozumi's PCP-bis(phosphinite) pincer Pd complex at 110 °C only gave a 60% yield after 24 h [23]. Very recently, Protasiewicz reported that similar *m*-terphenyl anchored symmetrical PCP-bis(phosphinite) pincer Pd complexes could promote the CC coupling of aryl bromides with *p*-tolylboronic acid at 50 °C and the catalysis was thought to occur via a Pd(0)–Pd(II) catalytic cycle [40]. However, the coupled products were obtained in only moderate yields with 1 mol% of catalyst after 20 h in the case of bromobenzene and 2-bromotoluene (76% and 45%, respectively). In contrast, our newly developed phosphinito-containing non-symmetrical PCN Pd complex **2a** exhibited much higher catalytic activities at 50 °C and the corresponding products could be obtained in >99% yields with 1 mol% of catalyst only after 3 h (Table 4, entries 2 and 4). Furthermore, the PCN complex **2a** was found to be much more active than the symmetrical PCP complex **3** under certain

Table 6
Optimization of reaction conditions for the copper-free Sonogashira coupling of iodobenzene with phenylacetylene.



Entry	Solvent	Base	Time (h)	Temperature (°C)	Yields (%)[a]
1	CH_3CN	Et_3N	12	rt	40
2	CH_3CN	Et_3N	12	80	53
3	Pyrrolidine	–	12	100	64
4	Pyrrolidine	–	24	100	70
5	EtOH	$K_3PO_4 \cdot 7H_2O$	12	80	59
6	EtOH	Cs_2CO_3	12	80	79
7	MeOH	Cs_2CO_3	12	70	99
8[b]	MeOH	Cs_2CO_3	12	70	98

Reaction conditions: Catalyst **2a** (2 mol%), iodobenzene (0.5 mmol), phenylacetylene (0.75 mmol), base (1.0 mmol), solvent (3.0 mL), under air.
[a] Isolated yields.
[b] Catalyst **2a** (1 mol%).

circumstances. Based on the above observations, we thought that the higher activity of the non-symmetrical PCN Pd complexes **2** at reduced temperature might be attributed to the hemilable coordination of PCN ligands, which made it easier for complexes **2** to release the catalytically active Pd(0) species than the symmetrical PCP-bis(phosphinite) pincer Pd complexes.

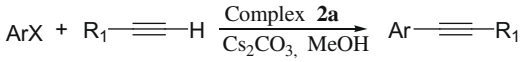
The activity of the obtained Pd complexes were also examined in the copper-free Sonogashira coupling. A brief optimization of experimental conditions for the reaction of iodobenzene with phenylacetylene is given in Table 6. Although using $K_3PO_4 \cdot 7H_2O$ as the base in EtOH at 50 °C in the above Suzuki reactions gave the best results, it only afford a low yield in the Sonogashira reaction (entry 5). Instead, Cs_2CO_3 in MeOH at 70 °C in the presence of 2 mol% **2a** provided the highest isolated yield of 99% (entry 7). When the loading of **2a** was decreased to 1 mol%, an excellent yield could also be obtained (entry 8).

To explore the scope of this system (1 mol% of complex **2a** as catalyst, Cs_2CO_3, MeOH), several aryl halides and alkynes were subjected to the coupling reactions, and the results are summarized in Table 7. 4-Iodotoulene, 4-chloroiodobenzene and 3-chloroiobenzene could be efficiently coupled with phenylacetylene, providing the corresponding products in excellent isolated yields at 70 °C after 12 h (entries 1–3). Arylation of 1-hexyne with iodobenzene also gave a high yield under the same conditions (entry 4). However, when 4-iodonitrobenzene and less reactive aryl bromides were used as the substrates, the coupled products were isolated in low yields (entries 5–8). Interestingly, it was found that the coupling of iodobenzene with phenylacetylene proceeded very effectively at room temperature under similar conditions (entries 9–10), while in the case of 4-iodotoluene, an unexpectedly obvious decrease in the yield was observed (entry 11).

2.3. Conclusions

We have conveniently synthesized a series of novel achiral and chiral PCN pincer palladium(II) complexes from commercially available starting materials in only two steps, of which the key step is one-pot phosphorylation/palladation reaction. The obtained complexes were successfully employed as efficient catalysts for the Suzuki and copper-free Sonogashira reactions. The advantages of the present catalytic process include easy synthesis of the catalyst, relative mild reaction conditions as well as convenient handling due to insensitivity to air and moisture of the system which allows the reactions to be conducted in the undried solvent under air. Synthesis of other chiral PCN pincer Pd(II) complexes as

Table 7
The copper-free Sonogashira coupling of aryl halides with terminal alkynes catalyzed by **2a**.



Entry	R_1	Aryl halide	Time (h)	Temperature (°C)	Yield (%)[a]
1	C_6H_5	4-Iodotoulene	12	70	96
2	C_6H_5	4-Chloroiodobenzene	12	70	98
3	C_6H_5	3-Chloroiodobenzene	12	70	91
4	n-C_4H_9	Iodobenzene	12	70	96
5	C_6H_5	4-Iodonitrobenzene	12	70	35
6	C_6H_5	4-Bromonitrobenzene	12	70	30
7	C_6H_5	4-Bromotoluene	12	70	39
8	C_6H_5	4-Bromoanisole	12	70	42
9	C_6H_5	Iodobenzene	24	rt	95
10	C_6H_5	Iodobenzene	12	rt	91
11	C_6H_5	4-Iodotoulene	12	rt	56

Reaction conditions: Catalyst **2a** (1 mol %), iodobenzene (0.5 mmol), alkyne (0.75 mmol), Cs_2CO_3 (1.0 mmol), MeOH (3.0 mL), under air.
[a] Isolated yields.

well as the use of the formed Pd compounds as catalysts are still in progress.

3. Experimental

3.1. General

The preparation reactions for the *m*-hydroxyaldimines and PCN pincer palladium complexes were carried out under nitrogen atmosphere. Toluene and triethylamine used in the aforementioned synthesis was distilled from sodium/benzophenone and CaH_2, respectively. The Suzuki and Sonogashira reactions were performed in the untreated solvents under air. The *m*-hydroxybenzaldimines **1a–c** [41], phenylboronic acid [42], 4-iodotoulene and 3-chloroiodobenzene [43] were prepared according to the literature methods. All other chemicals were used as purchased. Melting points were measured on a WC-1 microscopic apparatus and were uncorrected. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ with TMS as an internal standard for ^{1}H, ^{13}C NMR and 85% H_3PO_4 as the external standard for ^{31}P NMR. HRMS were measured on a Micromass Q-TOF mass spectrometry (Waters, Manchester, UK) with an ESI source.

3.2. Synthesis of (S)-3-(N-1-phenylethylimino)phenol

A mixture of *m*-hydroxybenzaldehyde (2.0 g, 16.4 mmol) and (*S*)-1-phenylethylamine (2.3 mL, 18.1 mmol) in toluene was refluxed in the presence of activated Al_2O_3 under nitrogen atmosphere. The reaction was monitored by IR spectra until the C=O absorption (1668 cm^{-1}) in *m*-hydroxybenzaldehyde disappeared. The reaction mixture was carefully filtered and the filtrate was reduced to dryness to afford **1d** as a yellow oil, which was used for the next step without further purification. 3.1 g, 82% yield. $[\alpha]_D^{20}$ +74 (c 0.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H, C*H*=N), 7.38 (d, J = 7.7 Hz, 2H, Ar-H), 7.31 (t, J = 7.5 Hz, 2H, Ar-H), 7.26–7.20 (m, 4H, Ar-H), 6.85–6.83 (m, 1H, Ar-H), 4.55 (q, J = 6.6 Hz, 1H, CH), 1.59 (d, J = 6.6 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.0, 156.2, 144.5, 137.4, 129.8, 128.5, 127.0, 126.7, 121.3, 118.3, 114.3, 69.5, 24.2. IR (KBr): ν 3039, 2971, 2927, 2871, 1643, 1590, 1453, 1272, 1234, 775, 695 cm^{-1}. HRMS (positive ESI): $[M+H]^+$ calcd for $C_{15}H_{16}NO$: 226.1232, found: 226.1234.

3.3. General procedure for the synthesis of PCN pincer palladium complexes

To a stirred solution of **1a–d** (0.55 mmol) and triethylamine (93 μL, 0.66 mmol) in toluene (5 mL) was added diphenylchlorophosphine or diisopropylchlorophosphine (0.66 mmol) under N_2 atmosphere at rt. The resultant mixture was refluxed for 1 h. $PdCl_2$ (97 mg, 0.55 mmol) was then added, and the reaction mixture was refluxed for another 5 h. After cooling, filtration, and evaporation, the residue was purified by preparative TLC on silica gel plates eluting with CH_2Cl_2 to afford the corresponding PCN pincer complexes **2a–e**.

[2-{*N*-(*m*-chlorophenyl)imino}-6-(diphenylphosphinoxy)phenyl] chloropalladium(II) (**2a**): 127 mg, 46% yield, pale yellow solids. M.p. 244–245 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 4.4 Hz, 1H, C*H*=N), 8.06–8.02 (m, 4H, Ph-H), 7.55–7.47 (m, 6H, Ph-H; 2H, Ar-H), 7.36 (t, J = 8.0 Hz, 1H, Ar-H), 7.29 (d, J = 8.0 Hz, 1H, Ar-H), 7.23 (d, J = 7.4 Hz, 1H, Ar-H), 7.16 (app t, J = 7.7 Hz, 1H, Ar-H), 7.03 (d, J = 8.0 Hz, 1H, Ar-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 174.4, 174.3, 162.7, 162.6, 155.3, 149.1, 145.9, 134.9, 133.1, 132.9, 132.8, 132.5, 132.3, 132.2, 130.3, 129.4, 129.3, 128.3, 127.6, 124.2, 123.1, 122.8, 116.4, 116.2. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 155.3. IR (KBr): ν 3054, 1571, 1540, 1470, 1427, 1226, 1109, 910, 824, 689 cm^{-1}. HRMS (positive ESI): $[M-Cl]^+$ calcd for $C_{25}H_{18}ClNOPPd$: 519.9849, found: 519.9858.

[2-(*N*-phenylimino)-6-(diphenylphosphinoxy)phenyl]chloropalladium(II) (**2b**): 128 mg, 45% yield, pale yellow solids. M.p. 258–259 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 4.6 Hz, 1H, C*H*=N), 8.00–7.95 (m, 4H, Ph-H), 7.47–7.39 (m, 8H, Ph-H), 7.36 (t, J = 7.8 Hz, 2H, Ph-H), 7.25 (t, J = 7.4 Hz, 1H, Ph-H), 7.14 (d, J = 7.4 Hz, 1H, Ar-H), 7.07 (app t, J = 7.7 Hz, 1H, Ar-H), 6.94 (d, J = 7.9 Hz, 1H, Ar-H). ^{13}C{^{1}H} NMR (100 MHz, DMSO): δ 176.4, 161.5, 153.9, 147.9, 146.4, 133.1, 132.5, 131.9, 131.7, 131.5 , 129.5, 129.4, 128.8, 127.8, 127.7, 124.9, 123.5, 115.9, 115.7. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 155.4. IR (KBr): ν 3053, 1576, 1543, 1484, 1428, 1350, 1309, 1227, 1192, 1157, 1049, 1026, 875, 816, 780, 748, 697 cm^{-1}. HRMS (positive ESI): $[M-Cl]^+$ calcd for $C_{25}H_{19}NOPPd$: 486.0239, found: 486.0233.

[2-(*N*-isopropylimino)-6-(diphenylphosphinoxy)phenyl]chloropalladium(II) (**2c**): 130 mg, 48% yield, pale yellow solids. M.p. 228–229 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 5.6 Hz, 1H, C*H*=N), 8.05–8.00 (m, 4H, Ph-H), 7.52–7.46 (m, 6H, Ph-H), 7.11–7.05 (m, 2H, Ar-H), 6.93 (d, J = 7.5 Hz, 1H, Ar-H), 4.25–4.21 (m, 1H, C*H*$(CH_3)_2$), 1.50 (d, J = 6.5 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR

(100 MHz, $CDCl_3$): δ 170.1, 170.0, 162.1, 162.0, 153.5, 146.3, 133.1, 132.6, 132.1, 131.8, 131.7, 128.9, 128.8, 126.8, 122.0, 114.6, 114.4, 60.0, 22.5. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 152.6. IR (KBr): ν 3053, 2969, 2930, 2870, 1596, 1550, 1429, 1319, 1230, 1150, 1109, 814, 745, 691 cm^{-1}. HRMS (positive ESI): $[M-Cl]^+$ calcd for $C_{22}H_{21}NOPPd$: 452.0396, found: 452.0402.

[2-{*N*-(*m*-chlorophenyl)imino}-6-(diisopropylphosphinoxy)phenyl] chloropalladium(II) (**2d**): 125 mg, 47% yield, pale yellow solids. M.p. 190–191 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, J = 3.9 Hz, 1H, C*H*=N), 7.55–7.52 (m, 1H, Ar-H), 7.48 (t, J = 2.0 Hz, 1H, Ar-H), 7.37 (app t, J = 8.0 Hz, 1H, Ar-H), 7.30–7.27 (m, 1H, Ar-H), 7.19 (d, J = 7.4 Hz, 1H, Ar-H), 7.11 (dt, J = 0.9, 7.8 Hz, 1H, Ar-H), 6.88 (d, J = 8.0 Hz, 1H, Ar-H), 2.56–2.47 (m, 2H, C*H*$(CH_3)_2$), 1.47 (d, J = 7.1 Hz, 3H, CH(C*H*$_3)_2$), 1.42 (d, J = 7.1 Hz, 3H, CH(C*H*$_3)_2$), 1.36 (d, J = 7.0 Hz, 3H, CH(C*H*$_3)_2$), 1.32 (d, J = 7.0 Hz, 3H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.2, 163.6, 153.3, 148.8, 145.6, 134.4, 129.9, 127.8, 126.8, 123.4, 122.6, 122.4, 115.0, 114.8, 29.7, 29.6, 29.3, 17.4, 17.3, 16.7. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 204.4. IR (KBr): ν 3067, 2969, 2926, 2869, 1575, 1544, 1457, 1424, 1351, 1227, 910, 821, 787, 760, 688 cm^{-1}. HRMS (positive ESI): $[M-Cl]^+$ calcd for $C_{19}H_{22}ClNOPPd$: 452.0162, found: 452.0166.

[(*S*)-2-{(*N*-1-phenylethyl)imino}-6-(diphenylphosphinoxy)phenyl] chloropalladium(II) (**2e**): 145 mg, 48% yield, pale yellow solids. M.p. 132–133 °C. $[\alpha]_D^{20}$ −66 (c 0.23, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.07–7.99 (m, 4H, Ph-H), 7.82 (d, J = 5.6 Hz, 1H, C*H*=N), 7.56–7.33 (m, 11H, Ph-H), 7.04 (app t, J = 7.7 Hz, 1H, Ar-H), 6.94–6.92 (m, 2H, Ar-H), 5.61–5.60 (m, 1H, CH), 1.86 (d, J = 6.9 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.0, 161.9, 161.8, 153.7, 146.2, 139.5, 133.1, 132.6, 132.5, 132.2, 131.7, 131.6, 129.0, 128.8, 128.6, 128.1, 126.7, 122.3, 114.7, 114.6, 63.6, 20.7. $^{31}P\{^1H\}$ NMR(162 MHz, $CDCl_3$): δ 154.1. IR (KBr): ν 3054, 2968, 2928, 2869, 1593, 1433, 1231, 1154, 1107, 825, 745, 698 cm^{-1}. HRMS (positive ESI): $[M-Cl]^+$ calcd for $C_{27}H_{23}NOPPd$: 514.0552, found: 514.0547.

3.4. General procedure for Suzuki cross-coupling reactions

A 5 mL round-bottom flask was charged with ArBr (0.5 mmol), $ArB(OH)_2$ (0.6 mmol), complex **2a** (0.3 mol%), $K_3PO_4 \cdot 7H_2O$ (1 mmol), and EtOH (3 mL). The mixture was stirred at 50 °C for 10 h under air. After the mixture was cooled, solvent was removed on a rotary evaporator, and the product was isolated by thin layer chromatography. The purified products were identified by ^1H NMR spectra or comparison of the melting points with the literature data.

3.5. General procedure for Sonogashira cross-coupling reactions

Pincer complex **2a** (1 mol%) was added to a mixture of aryl iodide (0.5 mmol), phenylacetylene (0.75 mmol), Cs_2CO_3 (1 mmol) and MeOH (3 mL) in a 5 mL round-bottom flask open to the atmosphere. After it was stirred at reflux for 12 h, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexane or hexane/ethyl acetate) to afford the pure product. The purified products were identified by ^1H NMR spectra or comparison of the melting points with the literature data.

3.6. X-ray diffraction studies

Crystals of **2a** and **2b** were obtained by recrystallization from CH_2Cl_2/petroleum ether at ambient temperature. All diffraction data were collected with Rigaku-IV imaging plate area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The diffraction data were corrected for Lorentz and polarization factors. The structures were solved by direct methods and expanded using Fourier techniques and refined by full-matrix least-squares methods [44]. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. Their raw data were corrected and the structures were solved using the SHELXL-97 program [45].

4. Supplementary material

CCDC 701329 and 701328 contain the supplementary crystallographic data for complexes **2a** and **2b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/data_request/cif>.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (Nos. 20572102, 20872133) and the Innovation Fund for Outstanding Scholar of Henan Province (No. 074200510005) for financial support of this work.

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