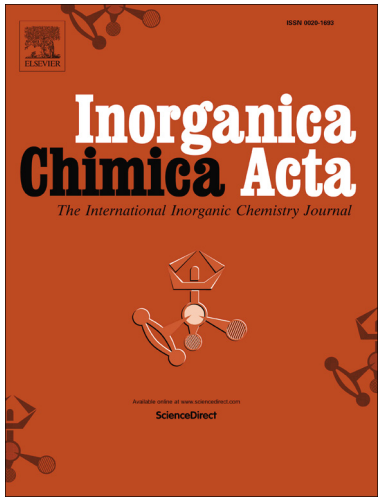

Research paper

Novel phosphorus-coordinated palladium(II) complexes derived from 3,5-disubstituted-*1H*-1,2,4-diazaphospholes: synthesis and catalytic application in Suzuki-Miyaura cross-coupling reactions

Xuefeng Jia, Fang Zhao

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Novel phosphorus-coordinated palladium(II) complexes derived from 3,5-disubstituted-*1H*-1,2,4-diazaphospholes: synthesis and catalytic application in Suzuki-Miyaura cross-coupling reactions

Xuefeng Jia,* Fang Zhao

School of Chemical and Material Science, Shanxi Normal University, Linfen, 041004, China

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ABSTRACT

Four novel phosphorus-coordinated palladium(II) complexes(**I-IV**) were easily prepared by the reaction of 3,5-disubstituted-*1H*-1,2,4-diazaphospholes with $Pd(CH_3CN)_2Cl_2$ at room temperature and characterized. The catalytic activity of palladium(II) complexes was further evaluated in Suzuki-Miyaura reaction of aryl halides with arylboronic acids, giving the biphenyl derivatives in good yields.

1. Intrduction

Palladium-catalyzed Suzuki-Miyaura reactions are one of the most versatile methods for the formation of C-C bonds in synthetic organic chemistry [1]. Over the past decades, special attention has been concentrated on synthesis of different palladium complexes and their activity in Suzuki-Miyaura coupling reactions. For example, N-heterocyclic carbene-based palladium complexes have proved to be excellent catalysts for C-C coupling reactions of organic halides with arylboronic acids [2-3]. Various pincer-type palladium complexes containing tridentate N-donor ligands have also been synthesized and applied to this reaction [4-5]. Besides that, many phosphine-based ligands were successfully used for palladium-catalyzed Suzuki-Miyaura cross-coupling reactions [6-8]. In 2010, Buchwald and co-worker reported the synthesis of 2-aminobiphenyl-derived palladium complexes with XPhos ligands and their application in Suzuki-Miyaura reactions [9]. Subsequently, the palladium complexes with biaryl-like KITPHOS and dihydro-KITPHOS monophosphines ligands were used for these coupling reactions by Doherty's group [10]. In 2012, Fernández and Lassaletta documented phosphino hydrazones as efficient ligands in the palladium-catalyzed asymmetric Suzuki-Miyaura reactions [11]. In addition, the air-stable $PdCl_2\{P^tBu_2(p\text{-}NMe_2\text{-}Ph)\}_2$ complexes were also employed in the cross-coupling reactions of aryl/heteroaryl chlorides with arylboronic acids [12] or potassium dioxolanylethyltrifluoroborate [13] as coupling partners. Yamamoto's group further developed the coupling reaction of tetrabutylammonium 2-pyridyltriolborate salts with various aryl/heteroaryl chlorides under $PdCl_2$dcpp {dcpp=1,3-bis (dicyclohexylphosphino)propane} and CuI/$MeNHCH_2CH_2OH$ combined systems [14]. Very recently, Schoenebeck and co-worker achieved the air-stable dinuclear iodine-bridged palladium(**I**) complex as the catalyst for Suzuki-Miyaura cross-coupling reactions [15].

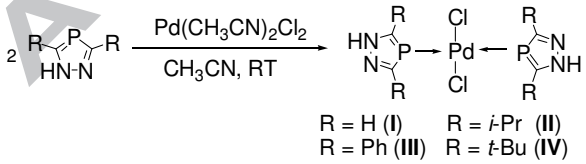
* Corresponding author. Tel.: +86-150-3435-8409; fax: +86-357-205-8711;
E-mail: jxfliu@163.com

Although significant progress has been achieved in this field, the exploration of new palladium catalyst in Suzuki-Miyaura Reactions remains highly desirable. Herein, we report the synthesis and structural characterization of several palladium complexes using 3,5-disubstituted-*1H*-1,2,4-diazaphospholes {H[3,5-R_2dp] (R = H, *i*-Pr, Ph, *t*-Bu)} [16] as heteroatom-containing monophosphine ligands and their catalytic performance in Suzuki-Miyaura reactions of aryl halides with arylboronic acids. To our knowledge, the use of a heteroatom-substituted phosphine as ligands for palladium-catalyzed Suzuki-Miyaura couplings is rarely studied [17]. More importantly, our palladium complexes are also air-stable and tunable catalyst, which may be conveniently applied in organic synthesis.

2. Results and discussion

*2.1. Synthesis and characterization of palladium complexes(**I-IV**)*

As described in **Scheme 1**, phosphorus-coordinated palladium(II) complexes **I-IV** were easily prepared by the reaction of H[3,5-R_2dp] (R = H, *i*-Pr, Ph, *t*-Bu) with $Pd(CH_3CN)_2Cl_2$ in anhydrous CH_3CN at room temperature. These complexes were isolated as solid with good yields (49% for **I**; 84% for **II**; 77% for **III**; 95% for **IV**, respectively) and characterized by NMR, IR spectroscopy, HRMS and elemental analysis. The ^{31}P NMR spectroscopy of **I-IV** revealed that the chemical shift of phosphorous atom had a slight changes in comparison to those of H[3,5-R_2dp] (R = H, *i*-Pr, Ph, *t*-Bu), which confirmed the formation of palladium(II) complexes bearing heteroatom-containing monophosphine ligands.



Scheme 1. Synthesis of palladium complexes **I-IV**

To further identify the coordination mode of *1H*-1, 2, 4-diazaphosphole with palladium atom, we tried to crystallize four palladium complexes in different solvents. Complex **I** is insoluble in common organic solvents such as CH_2Cl_2, $CHCl_3$ and CH_3CN, but slight soluble in DMSO. Complex **II** is well soluble in CH_2Cl_2 and complex **III-IV** may dissolve in CH_3OH. However, attempts to get single crystal of **I-III** at this stage were not successful. Fortunately, the single crystal of **IV** was obtained by slow evaporation of methanol solution at 4 °C and molecular structure was determined by X-ray diffraction [18]. X-ray structural analysis displayed that complex **IV** crystallized in monoclinic with P2(1)/c space group. As shown in **Fig. 1**, the central Pd ions take a precisely planar geometry with two phosphorus atoms from both H[3,5-*t*-Bu_2dp] and two chlorine atoms. The ligand of H[3,5-*t*-Bu_2dp] adopts monodentate coordination mode. The selected bond length(Å) and angle(°) for **IV** were listed in **Table 1**. The Cl(1)–Pd(1)–P(1) angle is 90.28(5)° and the Cl(1)–Pd(1)–P(1A) angle is 89.72(5)°. The bond angles of both Cl(1)–Pd(1)–Cl(1A) and P(1A)-Pd(1)-P(1) are 180.0°. These data demonstrate that Pd ions take a precisely planar geometry. The distance of Pd–P bond (2.2987 Å) in **IV** is longer than those in palladium(**II**) complexes with novel bidentate phosphine ligand (Pd–P 2.2308 Å) [8b] or Buchwald-Type secondary phosphine oxide ligands (Pd–P 2.2595 or 2.2735 Å) [8c]. But the Pd–Cl bond length (2.2877 Å) is shorter than the average distance of these palladium(**II**) complexes (Pd–Cl 2.338 Å or 2.376 Å) [8b, 8c] and 3,5-di-*tert*-butyl-*1H*-pyrazole-based palladium(**II**) complexes (Pd–Cl 2.3158 Å) [19].

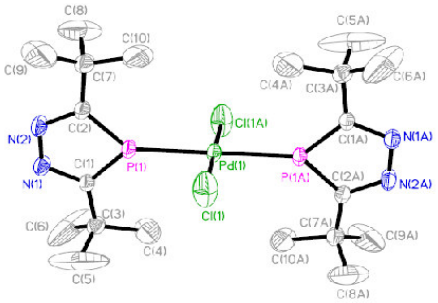


Fig. 1 X-ray crystal structure of palladium complex **IV**

Table 1

Selected bond length(Å) and angle(°) for IV

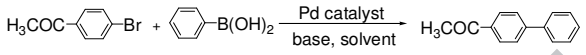
Pd(1)-P(1)	2.2987(11)	P(1)-Pd(1)-P(1A)	180.0
Pd(1)-Cl(1)	2.2877(16)	Cl(1)-Pd(1)-Cl(1A)	180.0

P(1)-C(2)	1.726(4)	Cl(1)-Pd(1)-P(1),	90.28(5)
P(1)-C(1)	1.728(4)	Cl(1)-Pd(1)-P(1A)	89.72(5)
N(1)-C(1)	1.327(5)	C(2)-P(1)-C(1)	91.4(2)
N(1)-N(2)	1.350(6)	C(2)-P(1)-Pd(1)	134.92(16)
N(2)-C(2)	1.336(5)	C(1)-P(1)-Pd(1)	133.62(15)

*2.2. Catalytic activity of palladium complexes (**I-IV**)*

Once palladium complexes **I-IV** were synthesized and characterized, we next investigate the catalytic activity of these complexes in Suzuki-Miyaura cross-coupling reaction. Initially, 4-bromoacetophenone (**1a**) and phenylboronic acid (**2a**) was chosen as model substrates to screen reaction conditions and the results were summaried in **Table 2**. When the reaction of **1a** with **2a** were carried out in DMF at 110°C using Cs_2CO_3 as a base in the presence of 8 mol% palladium complexes, we found that palladium complexes **I-IV** exhibited different catalytic activity and the desired product (**3aa**) were obtained in moderate to good yields (**Table 2**, entries 1-4). Among them, the activity of complex **IV** was greatly superior to other complexes **I-III**, which indicated that the substituted group (H, *i*-Pr, Ph, *t*-Bu) on *1H*-1, 2, 4-diazaphospholes had obvious effect on catalytic activity of palladium complexes. Subsequently, the impact of the base on this model reaction was investigated empolying the complexe **IV** as palladium catalyst. When Cs_2CO_3 was replaced by other base such as K_2CO_3, KOH and Et_3N, the yield of **3aa** sharply reduced ranging from 99%, 82%, 62% to 34% (**Table 2**, entries 4-7). Thus Cs_2CO_3 was best choice to obtain high yields. When the reaction was performed in DMSO at 110°C, **3aa** was isolated in 65% yield (**Table 2**, entry 8). So DMF should be better solvent. Then the effect of temperature on the reaction was also surveyed. The yield of coupled product obviously decreased after the reaction of **1a** with **2a** took place in DMSO or DMF at 160°C for 24 hours (**Table 2**, entries 9 and 10). Finally, we performed this coupling reaction at lower catalyst loading (5 mol% and 1 mol%), affording the desired product (**3aa**) with 92% and 44% yields respectively (**Table 2**, entries 11 and 12). As a result, the optimal reaction conditions were established as follows: Pd complex **IV** (8 mol%), Cs_2CO_3 (2 equiv), and **1a/2a** = 1:1.5 in DMF (1 mL) at 110°C for 24h.

Table 2
Screening for optimal reaction conditions [a]



1a **2a** **3aa**

Entry	Pd catalyst	Base	Solvent	T (°C)	Yield [b] (%)
1	**I**	Cs_2CO_3	DMF	110	71
2	**II**	Cs_2CO_3	DMF	110	51
3	**III**	Cs_2CO_3	DMF	110	54
4	**IV**	**Cs_2CO_3**	**DMF**	**110**	**99**
5	**IV**	K_2CO_3	DMF	110	82
6	**IV**	KOH	DMF	110	62
7	**IV**	Et_3N	DMF	110	34
8	**IV**	Cs_2CO_3	DMSO	110	65
9	**IV**	Cs_2CO_3	DMSO	160	54
10	**IV**	Cs_2CO_3	DMF	160	71
11 [c]	**IV**	Cs_2CO_3	DMF	110	92
12 [d]	**IV**	Cs_2CO_3	DMF	110	44

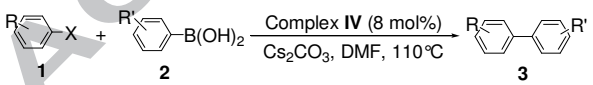
[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.225 mmol, 1.5 equiv), Pd catalyst (8 mol %), base (0.3 mmol, 2 equiv) in solvent (1.0 mL) at the indicated temperature for 24h.
[b] Isolated yield.
[c] Palladium complex **IV** (5 mol%) was used.
[d] Palladium complex **IV** (1 mol%) was used.

With an optimized catalyst system in hand, the substrate scope for palladium-catalyzed Suzuki-Miyaura coupling reaction was evaluated. As summarized in **Table 3**, the reaction of several aryl bromide bearing different groups with phenylboronic acid were firstly carried out. The experiment results demonstrated that aryl bromide with electron-withdrawing groups (4-acetyl, 4-formyl) exhibited high reactivity than those containing electron-donating groups (4-OMe, H) in this transformation (**Table 3**, entries 1, 2 vs entries 3, 4). Then a variety of arylboronic acids were employed as substrate to react with 4-bromoacetophenone (**1a**). Substrates with methyl group (**2b**), *tert*-butyl group (**2c**) and methoxy group (**2d**) at the *para*-position gave the corresponding products **3ab**-**3ae** in 76–94% yields (**Table 3**, entries 5-7). *Ortho*-methyl-substituted arylboronic acid (**2e**) also furnished the desired product

3ae with 86% yield (**Table 3**, entry 8). The lower yields of the products were obtained when substrates bearing electron-withdrawing group (4-F, 3-Cl) at the *para*- or *meta*-position were used (**Table 3**, entries 9-10). However, *meta*-nitro-substituted phenylboronic acid proved to be poor substrate under optimal conditions (**Table 3**, entry 11). But to our delight, the reaction of 1-naphthyl boronic acid (**2i**) with 4-bromoacetophenone (**1a**) led to the product **3ai** in 55 % yield (**Table 3**, entry 12). These results revealed that arylboronic acid with electron-donating substituents (4-OMe, 4-*t*-Bu, 2-Me) was favorable to this coupling reaction. Sequently, we performed the Suzuki–Miyaura reaction of 4-methoxyphenylboronic acid (**2d**) with 4-bromobenzaldehye (**1b**) and 4-bromoanisole (**1c**) under standard conditions, providing the product **3bd** and **3cd** in good yields (82% for **3bd**; 78% for **3cd**, respectively) (**Table 3**, entry 13 vs entry 15). Surprisely, the reaction of 3-chlorophenylboronic acid (**2g**) with **1b** afforded the coupling product **3bg** in 95% yield and 4-bromoanisole (**1c**) reacted with **2e** to give **3ce** in 91% yield (**Table 3**, entry 14 vs entry 16). These data indicated that steric hindrance of substituents on the aryl rings had obvious influence on substrate reactivity to a certain extent. Finally, the reactivity of aryl chloride was further explored. The reaction of 4-chloroacetophenone (**1e**) with several arylboronic acid such as **2a**, **2c**, **2d**, **2e** proceeded smoothly and offered the corresponding products in moderate to good yield (**Table 3**, entries 17-20).

Table 3

Palladium-catalyzed Suzuki-Miyaura coupling of aryl halides with different arylboronic acids [a]



Entry	1(R)	X	2(R')	3	Yield[b] (%)
1	**1a** (4-$COCH_3$)	Br	**2a** (H)	**3aa**	99
2	**1b** (4-CHO)	Br	**2a** (H)	**3ba**	88
3	**1c** (4-OCH_3)	Br	**2a** (H)	**3ca**	83
4	**1d** (H)	Br	**2a** (H)	**3da**	69
5	**1a** (4-$COCH_3$)	Br	**2b** (4-CH_3)	**3ab**	76
6	**1a** (4-$COCH_3$)	Br	**2c** (4-*t*-Bu)	**3ac**	77
7	**1a** (4-$COCH_3$)	Br	**2d** (4-OCH_3)	**3ad**	94
8	**1a** (4-$COCH_3$)	Br	**2e** (2-CH_3)	**3ae**	86
9	**1a** (4-$COCH_3$)	Br	**2f** (4-F)	**3af**	72
10	**1a** (4-$COCH_3$)	Br	**2g** (3-Cl)	**3ag**	72
11	**1a** (4-$COCH_3$)	Br	**2h** (3-NO_2)	**3ah**	ND [c]
12	**1a** (4-$COCH_3$)	Br	**2i**(1-Naphthyl boronic acid)	**3ai**	55
13	**1b** (4-CHO)	Br	**2d** (4-OCH_3)	**3bd**	82
14	**1b** (4-CHO)	Br	**2g** (3-Cl)	**3bg**	95
15	**1c** (4-OCH_3)	Br	**2d** (4-OCH_3)	**3cd**	78
16	**1c** (4-OCH_3)	Br	**2e** (2-CH_3)	**3ce**	91
17	**1e** (4-$COCH_3$)	Cl	**2a** (H)	**3ea**	51
18	**1e** (4-$COCH_3$)	Cl	**2c** (4-*t*-Bu)	**3ec**	56
19	**1e** (4-$COCH_3$)	Cl	**2d** (4-OCH_3)	**3ed**	71
20	**1e** (4-$COCH_3$)	Cl	**2e** (2-CH_3)	**3ee**	48

[a] Reaction conditions: aryl halides **1** (0.15 mmol), arylboronic acid **2** (0.225 mmol, 1.5 equiv), Pd complex **IV**(8 mol %), Cs_2CO_3 (0.3 mmol, 2 equiv) in DMF (1.0 mL) at 110°C for 24h.

[b] Isolated yield.

[c] ND = not detected.

3. Experimental

3.1 General information

All the reactions were performed under argon atmosphere using standard vacuum line techniques. The solvents were dried and distilled according to standard method. 3,5-disubstituted-*1H*-1,2,4-diazaphospholes were synthesized according to reported procedure [16c]. $Pd(CH_3CN)_2Cl_2$ was used immediately after preparation. Preparative thin layer chromatography was carried out on GF-254 silica gel using petroleum ether/ethyl acetate as the eluent. The ^1H, ^{31}P and ^{13}C NMR spectra were obtained on 600 MHz spectrometers. The NMR data were reported as chemical shift (δ ppm) and coupling constants (*J*) were recorded in hertz unit (Hz). C, H, and N analyses were measured on an elemental analyzer. Infrared (IR) spectra were recorded as KBr pellets on FT-IR spectrometer. HRMS were measured on a TOF mass analyzer. The X-ray diffraction data of complex **IV** were collected with Oxford diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by the direct method and refined through full-matrix least-squares techniques method on F^2 using the SHELXL 2014 crystallographic software package[20].

3.2 Syntheses

*3.2.1 Synthesis of Pd{H[3,5-H_2dp]}$_2Cl_2$(**I**)*

In a 100ml Schlenk flask, $PdCl_2$ (89 mg, 0.5 mmol) was dissolved in 20 ml of anhydrous CH_3CN and the mixture was refluxed for one hour to obtain the yellow solution of $Pd(CH_3CN)_2Cl_2$. After cooling to room temperature, a solution of *1H*-1,2,4-diazaphospholes {H[3,5-H_2dp]} (95 mg, 1.1 mmol) in anhydrous CH_3CN (10 mL) was added. A yellow-green precipitate appeared immediately and the reaction mixture was stirred for 12 hours at room temperature. The resulting precipitate was filtered off, washed with CH_3CN (5 mL×3) and dried under vacuum. The product was afforded as yellow-green solid. No ^{1}H and ^{13}C NMR data are available due to the low solubility of complex **I** in common organic solvents, but ^{31}P NMR data was obtained. Yield: 85 mg, 49%; m.p. 208-210℃; ^{31}P NMR (242 MHz, DMSO-d_6): δ 82.1. IR (KBr): υ 3453, 3167, 3095, 2941, 1631, 1179, 1048, 655 cm^{-1}. HRMS (ESI): m/z calcd for $C_4H_6Cl_2N_4P_2PdNa$: 370.8378 $[M+Na]^+$; found 370.8382. Anal. Calcd for $C_4H_6N_4P_2PdCl_2$: C, 13.75; H, 1.73; N, 16.04; found: C, 14.03; H, 1.68; N, 15.96.

*3.2.2 Synthesis of Pd{H[3,5-iPr_2dp]}$_2Cl_2$(**II**)*

As described for **I,** palladium complexe **II** was prepared by the same procedure with $PdCl_2$ (53 mg, 0.3 mmol) and 3,5-di-*iso*-propyl-*1H*-1,2,4-diazaphospholes {H[3,5-iPr_2dp]} (102 mg, 0.6 mmol). The product was afforded as pale-yellow solid. Yield: 130 mg, 84%; m.p. 180-182℃; ^{1}H NMR (600 MHz, CD_2Cl_2): δ 12.87 (s, 2H, NH), 4.58-4.53 (m, 2H), 2.95-2.89 (m, 2H), 1.55 (d, *J* = 7.2 Hz, 12H), 0.93 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ 33.87, 33.77, 29.55, 29.46, 25.05, 24.99, 24.33, 24.28; ^{31}P NMR (242 MHz, CD_2Cl_2): δ 78.0. IR (KBr): υ 3441, 3122, 2967, 2930, 2866, 1627, 1463, 1390, 1043, 721 cm^{-1}. HRMS (ESI): m/z calcd for $C_{16}H_{30}Cl_2N_4P_2PdNa$: 539.0256 $[M+Na]^+$; found 539.0252. Anal. Calcd for $C_{16}H_{30}N_4P_2PdCl_2$: C, 37.12; H, 5.84; N, 10.82; found: C, 37.45; H, 5.62; N, 11.05.

*3.2.3 Synthesis of Pd{H[3,5-Ph_2dp]}$_2Cl_2$(**III**)*

As described for **I,** palladium complexe **III** was prepared by the same procedure with $PdCl_2$ (53 mg, 0.3 mmol) and 3,5-diphenyl-*1H*-1,2,4-diazaphospholes {H[3,5-Ph_2dp]} (143 mg, 0.6 mmol). The product was afforded as dark-red solid. Yield: 150 mg, 77%; m.p. 170-172℃; ^{1}H NMR (600 MHz, CD_3OD): δ 7.84 (d, *J* = 6.6 Hz, 5H), 7.44 (d, *J* = 7.2 Hz, 7H), 7.41-7.37 (m, 5H), 7.31 (dd, *J* = 1.2, 7.2 Hz, 2H), 7.26 (t, *J* = 6.6 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD): δ 129.1, 128.7, 128.6, 126.1, 126.0; ^{31}P NMR (242 MHz, DMSO-d_6): δ 72.9. IR (KBr): υ 3450, 3140, 2958, 2858, 1627, 1490, 1454, 1271, 1007, 752, 688 cm^{-1}. HRMS (ESI): m/z calcd for $C_{28}H_{22}Cl_2N_4P_2PdNa$: 674.9630 $[M+Na]^+$; found 674.9635. Anal. Calcd for $C_{28}H_{22}N_4P_2PdCl_2$: C, 51.44; H, 3.39; N, 8.57; found: C, 51.18; H, 3.52; N, 8.47.

*3.2.4 Synthesis of Pd{H[3, 5-tBu_2dp]}$_2Cl_2$(**IV**).*

As described for **I,** palladium complexe **IV** was prepared by the same procedure with $PdCl_2$ (67 mg, 0.38 mmol) and 3,5-di-*tert*-butyl-*1H*-1,2,4-diazaphospholes {H[3,5-tBu_2dp]} (150 mg, 0.76 mmol). The product was afforded as orange-yellow solid. Suitable single crystal for X-ray diffraction was obtained by the slow evaporation of the methanol solution of **IV** at 4 °C. Yield: 207 mg, 95%; m.p. 177-179℃; ^{1}H NMR (600 MHz, CD_3OD): δ 1.59 (s, 18H), 1.38 (s, 18H); ^{13}C NMR (150 MHz, CD_3OD): δ 30.71; ^{31}P NMR (242 MHz, CD_3OD): δ 64.0. IR (KBr): υ 3429, 3177, 2958, 2866, 1627, 1472, 1363, 1253, 1099, 1016, 807 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{38}Cl_2N_4P_2PdNa$: 595.0882 $[M+Na]^+$; found 595.0885. Anal. Calcd for $C_{20}H_{38}N_4P_2PdCl_2$: C, 41.86; H, 6.67; N, 9.76; found: C, 41.72; H, 6.54; N, 9.95.

3.3 General procedure for palladium-catalyzed Suzuki-Miyaura coupling reactions

A 25 mL Schlenk tube was charged with aryl halides **1** (0.15 mmol), arylboronic acids **2** (0.225 mmol, 1.5 equiv), Cs_2CO_3 (0.3 mmol, 2 equiv), Pd catalyst (8 mol%) and DMF (1.0 mL). Then the tube was sealed and heated to 110°C in oil bath. After stirring for 24h, the reaction mixture was cooled and extracted with ethyl acetate. The combined organic phase was concentrated and purification of the residue by preparative thin layer chromatography furnished the corresponding product **3**.

4. Conclusion

In summary, we have reported on synthesis, characterization and catalytic studies of four novel

palladium(II) complexes(**I-IV**) ligated with phosphorus atom of both 3,5-disubstituted-*1H*-1,2,4-diazaphospholes heterocycles and two chlorine atoms. The crystal structure of complex **IV** was confirmed by X-ray diffraction. The palladium complexes **IV** proved to be better catalyst for Suzuki-Miyaura cross-coupling reactions, which could tolerate many functional groups such as Me, MeO, *t*-Bu, F, Cl, 1-naphthyl, 4-acetyl, 4-formyl and provide the corresponding products in good to excellent yields (up to 99%).

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Appendix A. Supplementary data

Supplementary data (comparison on ^{31}P NMR chemical shift, crystallographic data of palladium complex **IV**, characterization data of Suzuki Product **3**, and NMR spectral copies of all products) related to this article can be found at http://dx.doi.org/10.1016/

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Graphical Abstract

Novel phosphorus-coordinated palladium(II) complexes derived from 3,5-disubstituted-*1H*-1,2,4-diazaphospholes: synthesis and catalytic application in Suzuki-Miyaura cross-coupling reactions

Xuefeng Jia, * Fang Zhao

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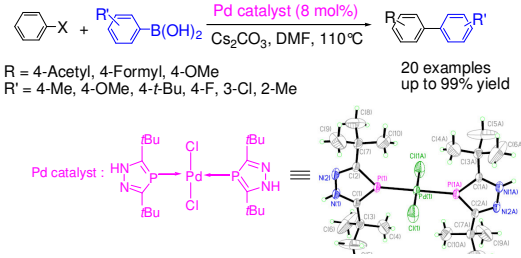

Highlights of this manuscript are listed as follows:

1. **Employing 3,5-disubstituted-*1H*-1,2,4-diazaphospholes as heteroatom-containing monophosphine ligands**
2. **The formation of novel phosphorus-coordinated palladium(II) complexes**
3. **Good catalytic activity and wide substrate scope**