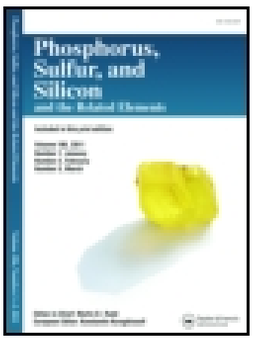

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Pd(II) Complexes of Novel Phosphine Ligands: Synthesis, Characterization and Catalytic Activities on Heck Reaction

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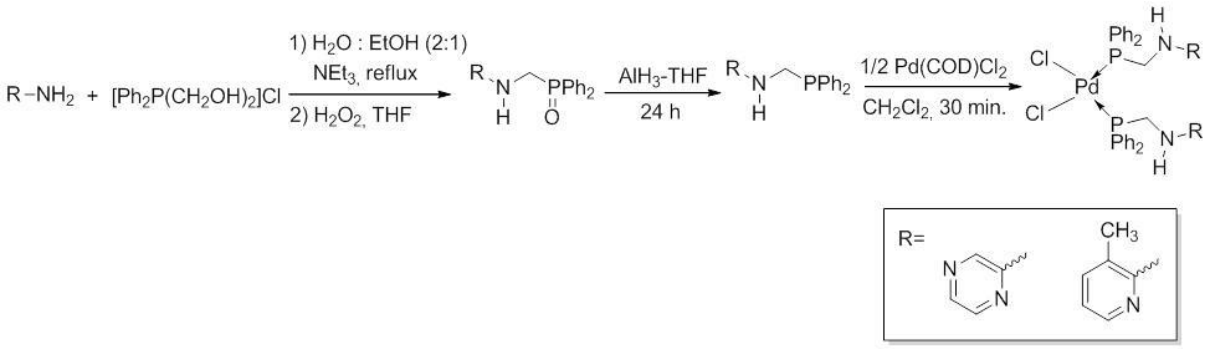
Shortened title: New Pd(II) Complexes for Heck Reaction

ABSTRACT

Novel phosphine oxides, (((3-methylpyridin-2-yl)amino)methyl)diphenylphosphine oxide (**1**) and diphenyl((pyrazin-2-ylamino)methyl)phosphine oxide (**2**), were synthesized and characterized. Phosphines ligands (**3** and **4**) were obtained by the reduction of **1** and **2** with AlH_3, monitored by ^{31}P NMR spectroscopy. Pd(II) complexes of **3** and **4** were synthesized and characterized (**5** and **6**). The catalytic activity of **5** and **6** was tested on the reaction of styrene with both activated and deactivated aryl bromides in air. The results of the catalytic experiments were discussed through DFT calculations.



Keywords: phosphine ligands, palladium complexes, Heck reaction, DFT calculations.

INTRODUCTION

Palladium-catalyzed cross-coupling reactions leading to the formation of carbon-carbon bonds are among the most powerful tools in organic synthesis.[1,2] Mizoroki-Heck cross-coupling reaction is a widely used method to couple aryl halides with terminal olefins to form cinnamates and stilbenes, which are of industrial importance.[3] It is known that palladium complexes, containing phosphine ligands, which combine both good donor strength and π-accepting capacity, have a high catalytic activity in Mizoroki-Heck cross-coupling reactions.[4]

In this study, two new phosphine oxides were synthesized and characterized. Their reduction products were used as ligands to prepare Pd(II)-phosphine complexes. The catalytic activity of Pd(II)-phosphine complexes was investigated on Heck Reaction of styrene with both activated and deactivated aryl bromides in air. The results of the catalytic experiments were discussed through DFT calculations.

RESULTS AND DISCUSSION

Synthesis

The Mannich condensation is a powerful tool to prepare aminomethylphosphines by the reaction of hydroxymethylphosphines with aliphatic or aromatic amines. This procedure provides a standard route to linear, branched and cyclic aminophosphines[5-7]. In contrast to aliphatic and aromatic amines, aminopyridines react sluggishly and long reaction times are required[8]. This may be due to either reducing the nucleophilicity of the amino group by the pyridine ring or tautomerism phenomena on the aminopyridine. In the literature, although some aminopyridinemethylphosphines can be isolated in moderate yields[8,9], in our hands, 3-

methylpyridin-2-amine (**3**) and pyrazin-2-amine (**4**) derivatives of aminomethylphosphines non-isolable. Several attempts were to isolate the free phosphine ligands were unsuccessful. In order to perform characterization properly, the crude product was treated with H_2O_2, and the oxide forms of the desired ligands (**1** and **2**) were isolated in fair yields. The route of synthesis was given in Scheme 1.

Reduction of phosphine oxides can be achieved by numerous ways[10]. The method[11], which uses alane (AlH_3) as reducing agent, is easy to perform, is very high yielding and does not require an aqueous workup, was applied in this work to reduce phosphine oxides. Reduction processes were achieved in >95% yield based on the ^{31}P NMR and 84-88% based on the product mass (Scheme 1).

Metal complexes (**5** and **6**) were synthesized immediately, by the reaction of $Pd(COD)Cl_2$ with phosphines in 2:1 molar ratio at room temperature.

Characterization

Oxide forms of the ligands (**1** and **2**), and metal complexes (**5** and **6**) were characterized by ^{31}P, ^{13}C, ^{1}H NMR, FT-IR spectroscopies and elemental analysis.

The ^{31}P NMR spectra of **1** and **2** showed single resonances at 31.0 and 30.2 ppm, respectively, which were in consistent with those reported tertiary phosphine oxides[9c]. In the ^{13}C NMR spectra, doublets at 40.3 (J = 77.4 Hz) and 40.3 (J = 78.9 Hz) ppm are indicative for the N-CH_2-P bound formation, for **1** and **2** respectively. Similarly, the peaks in the ^{1}H NMR spectra that are found at 4,47 (d, J_{PH} = 5.2 Hz)(**1**) and 4.42 (t, J_{PH} = 6.0 Hz) ppm (**2**) are also supported the N-CH_2-P bound formation. Furthermore, the peaks in the ^{1}H NMR spectra at 6.59(**1**) and 6.56(**2**)

ppm (N*H*) are confirmed the presence of only one Ph_2PCH_2 group maintained on the molecule[8, 9].

The IR spectrum of **1** and **2** showed characteristic weakly absorbing stretching vibrations of ν(NH) at 3250 $cm^{-1}$and 3258 cm^{-1} and strong absorptions of ν(P=O) at 1178 cm^{-1} and 1164 cm^{-1} respectively.

After the reduction process of phosphine oxides, the peaks that are observed in the ^{31}P NMR spectra at 31.0 **(1)** and 30.2 **(2)** ppm, were shifted to -16.7 ppm (**3)** and -17.0 (**4)** which are characteristic for mono-substituted aminomethylphosphines[8, 9].

In the ^{31}P NMR spectra of **5** and **6**, the peaks at 25.5 and 26.5 ppm were demonstrated the coordination of the ligands to the Pd(II) center, free phosphines have -16.7 ppm and -17.0 ppm for **3** and **4,** respectively[8,9]. Durran *et al.* have shown that, by spectroscopic and single crystal XRD measurements, analogues of **3** and **4** prefer phosphorus coordination in a *cis* mode, when the ligand : metal molar ratio was 2 : 1[8,9a,b]. The spectroscopic results obtained in our work, are in consistent with the literature and it can be assumed that phosphines are bound to Pd(II) center in a cis manner. The structures of the complexes are given in Scheme 1.

Conventionally, comparing the spectroscopic data of the ligand and their metal complex is more preferred way to indicate the electronic differentiation on the structure. However, some differences can also be detected between the phosphine oxides and the metal-phosphine complexes, which can be connected by the back-donation phenomena of the phosphine ligands[12].

It can be noticed that in the ^{31}P NMR spectra, the formation of metal complexes resulted in increased electron density on phosphorus atoms (**5**, 25.5 ppm and **6**, 26.5 ppm), compared to the

oxide forms (**1**, 31.0 ppm and **2**, 30.2 ppm). Similarly, the increase of the electron density on phosphorus atoms reflected in the ^{13}C NMR spectra, as the shifting the peaks of ipso-carbon of phenyl ring (133.9 ppm, J = 94.4 Hz, **5**; 132.5 ppm, J = 104.2 Hz, **6**) as well as N-*C*-P carbon of methyl backbone (39.9 ppm, J = 69.4 Hz, **5**; 40.3 ppm, J = 65.1 Hz, **6**), to the upfield region and coupling constants decreased. Finally, in the ^{1}H NMR spectra, N-CH_2-P protons were observed as singlet at 4.46 ppm (**5**) and 4.31 ppm (**6**) which were shifted to the upfield region, compared with the oxide forms (4.47 ppm, [d, J = 5.2 Hz] **1;** 4.42 [t, J = 6.0 Hz] **2**)

The IR spectra of **5** and **6** showed bands centered at 3327 cm^{-1}, 3353 cm^{-1} and 327- 327 cm^{-1} indicative of ν(NH) and ν(Pd-Cl), respectively. P=O bound stretching frequencies at 1178 cm^{-1} (**1**) and 1164 cm^{-1} (**2**) are disappeared in the IR spectra of **5** and **6**, as well.

Catalytic activity

Palladium-catalyzed cross-coupling reactions have been proved extremely powerful synthetic tools. The effectiveness of the palladium catalyst depends on the ligand coordinated to the palladium atom[13]. The rate of coupling, as its well known, also depends on parameters such as solvent, base and reaction temperature. In this study, in order to optimize the reaction conditions bromobenzene was chosen as a model substrate for styrene. Four different bases and two different solvents were tested with a 0.4% mol catalyst ratio at 140 °C. After 3 h, the best results were obtained in DMF at 140 °C with 1.2 eq. Na_2CO_3 and the 0.4% mol catalyst ratio and these conditions were chosen to investigate the catalytic activity of complexes on the reaction of styrene with seven different aryl bromides. The results of the optimization experiments are summarized in Table 1.

The catalytic activity of **5** and **6** was investigated in the reaction of styrene with activated and deactivated aryl bromides. In the light of optimization experiments, minimum reaction time set at 3 hours and reactions were continued until the complete conversion. Good to excellent yields were obtained (Table 2). In the reactions with activated aryl bromides, **5** accelerated the reaction more than **6** (Table 2, Entry 1-3) and in the reaction with deactivated one, 2-bromo-6-methoxynaphthalene (Entry 4), as well. On the other hand, it can be considered that **6** is more selective than **5**. In the case of 2-bromo-6-methoxynaphthalene, only the desired product was obtained. The results are summarized in Table 2.

DFT Calculations

Structurally similar Pd(II) complexes (**5** and **6**) were showed different catalytic activities on Heck reaction. In order to understand the reason of this, we focused on Heck reaction mechanism. It is widely accepted that oxidative addition is the rate limiting step on Heck reaction. In this step zero-valent palladium species, formed during the pre-activation process[3,4,13], reacts with aryl halides. In the literature, the zero-valent palladium was usually described as di-coordinated Pd^0 complexes.

Complex **5** and **6** are not only monophosphines but also have nitrogen donors which can be coordinate to the metal center. We were supposed that tetra-coordinated Pd^0 (**5b** and **6b**) complexes, which are catalytically inactive, (Scheme 2) can be formed during the pre-activation process. In order to investigate this suggestion, mentioned di- and tetra- coordinated Pd^0 complexes are optimized at B3LYP/6-31G(d)(LANL2DZ) level in gas phase and thermodynamic parameters of relevant complexes are investigated in detail.

Optimized structures of complexes are represented in Figures S 15-S 18 (Supplemental Materials) and structural parameters are given in Table S 1. The most stable complexes for each equilibrium are determined by using total energy (E_{Total}), enthalpy (H) and Gibbs free energy (G). Additionally, equilibrium constants (K) for each transformation are predicted (Table S 2). Catalytic activity rankings of these complexes are investigated by using some quantum chemical parameters which are energy of HOMO (E_{HOMO}), energy gap between LUMO and HOMO (E_{GAP}), global hardness (η), global softness (σ), electronegativity (χ), electrophilicity index (ω), nucleophilicity index (N) and dipole moment (μ) (Table S 3).

According to the DFT calculations, **5b** and **6b** are probable species. However complex **5a** and **6a** are more stable complexes. Equilibrium constants of **5a** ⇌ **5b** and complex **6a** ⇌ **6b** are calculated as 0.984 and 0.857, respectively. These equilibrium constants were not indicated significant correlation between equilibrium constants and catalytic activities.

E_{HOMO} and nucleophilicity are the quantum chemical descriptors that usually associated with electron donating ability. High value of E_{HOMO} and nucleophilicity shows the tendency of electron transfer to appropriate molecule[14,15]. If E_{HOMO} and nucleophilicity are decisive for the catalytic reactivity in the oxidative addition step, **5a** should be a more active catalyst than **6a**, which is in agreement with the experimental results.

CONCLUSIONS

phosphines can be isolated in moderate yields but those pyridine/pyrazine containing phosphine ligands (**3**) and (**4)** were non-isolable. Fortunately, the oxide forms of the ligands **1** and **2** were properly isolated and characterized. Their palladium complexes (**5** and **6)** were synthesized by the reaction of phosphines (**3** and **4**), obtained by the reduction processes, with $CODPdCl_2$ at

room temperature in good yields. The catalytic activity of the complexes was tested on the Heck reaction. Good to excellent yields were obtained on the reaction of styrene with both activated and deactivated aryl bromides in air.

EXPERIMENTAL

All reactions were performed under argon, all chemicals and solvents were purchased from Aldrich and used directly without further purification unless otherwise stated. EtOH and de-ionized H_2O were degassed prior to use. CH_2Cl_2 was distilled under argon and stored 4 Å molecular sieve. THF and Et_2O were dried over sodium-benzophenonekethyl and distilled under argon. Bis(hydroxymethyl)diphenylphosphonium chloride[16], AlH_3-THF[13] and $PdCl_2(COD)$[17] were prepared according to literature procedures. IR spectra were recorded by using a Perkin Elmer FT-IR/FIR/NIR Spectrometer Frontier Spectrometer. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra were recorded on Bruker 400 MHz NMR Spectrometer with chemical shifts (δ) in ppm to high frequency of $SiMe_4$ and H_3PO_4, respectively. Elemental analysis were performed on LECO CHNS-932 with TCD detector. GC analyses were performed on a PerkinElmer Clarus 500 gas chromatograph equipped with a flame-ionization detector (FID) and a 30 m capillary column containing dimethylpolysiloxane stationary phase. ^{1}H, ^{13}C and ^{31}P NMR spectra of synthesized compounds are presented in Supplemental Materials (Figures S 1-S 14).

Synthesis

3-CH_3-py-2-$NHCH_2P(O)Ph_2$ (1): To a solution of bis(hydroxymethyl)diphenylphosphonium chloride (0.7630 g, 2.7 mmol) in EtOH:H_2O (2:1, 15 mL) NEt_3 (1.0 mL) was added followed by the appearance of cloudy solution. Then, 3-methylpyridin-2-amine (0.2808 g, 2.6 mmol) was

added and the mixture was refluxed for 36 h. After cooling to room temperature the mixture was extracted with CH_2Cl_2 (3 × 10 mL). Organic layer was separated and dried on $MgSO_4$, volatiles removed under reduced pressure and remaining oily residue was dissolved THF (5 mL). H_2O_2 (30%, 1 mL) was added to this solution and stirred for 24 h. White solid was obtained by adding n-hexane. Yield: 0.5424 g (64.7%) (**1).** IR : 3250 cm^{-1} (νNH), 1178 cm^{-1} (νP=O). ^{1}H NMR (400 MHz,) δ 8.05 (d, *J* = 4.8 Hz, 1H^{3}), 7.48 – 7.27 (m, 10H$^{12\text{-}21}$), 7.17 (d, *J* = 6.9 Hz, 1H^{1}), 6.59 (s, 1H^{7}), 6.53 (dd, *J* = 6.9, 5.2 Hz, 1H^{2}), 4.47 (d, *J* = 5.2 Hz, 2H^{8}), 2.04 (s, 3H^{22}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.6 (d, *J* = 4.3 Hz, C^{5}), 145.4 (C^{3}), 136.8 (C^{1}), 135.9 (d, *J* = 141.74 Hz, C$^{10, 11}$), 133.0 (d, *J* = 17.7 Hz, C$^{14, 19}$), 129.0 (d, *J* = 6.7 Hz, C$^{12, 16, 17, 21}$), 128.65 (d, *J* = 6.5 Hz, C$^{13, 15, 18, 20}$), 116.9 (C^{6}), 113.0 (C^{2}), 40.3 (d, *J* = 77.4 Hz, C^{8}), 16.6 (C^{22}). ^{31}P NMR (162 MHz,): δ 31.0 (s). Anal. Calcd for $C_{19}H_{19}N_2OP$: C, 70.80; H, 5.94; N, 8.69; Found: C, 70.94; H, 5.96 N, 9.00

pyz-2-NHCH$_2$P(O)Ph$_2$ (2): This compound was prepared by the same procedure described above for **1** and obtained as light yellow solid (0.5931 g). Yield : 64.0%. IR : 3258 cm^{-1} (νNH), 1164 cm^{-1} (νP=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.2 Hz, 1H^{3}), 7.89 (dd, *J* = 2.6, 1.4 Hz, 1H^{2}), 7.83 – 7.75 (m, 4H$^{12, 16, 17, 21}$), 7.73 (d, *J* = 2.8 Hz, 1H^{6}), 7.59 – 7.35 (m, 6H$^{13, 14, 15, 18, 19, 20}$), 6.56 (s, 1H^{7}), 4.42 (t, *J* = 6.0 Hz, 2H^{8}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2 (d, *J* = 5.9 Hz, C^{5}), 141.1 (C^{3}), 133.7 (d, *J* = 154.6 Hz, C$^{10, 11}$), 132.3 (d, *J* = 2.8 Hz, C$^{14, 19}$), 131.4 (C^{6}), 131.1 (d, *J* = 9.8 Hz, C$^{12, 16, 17, 21}$), 130.4 (C^{2}), 128.8 (d, *J* = 11.8 Hz, C$^{13, 15, 18, 20}$), 40.3 (d, *J* = 78.9 Hz, C^{8}). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2 (s). Anal. Calcd for $C_{17}H_{16}N_3OP$: C, 66.01; H, 5.21; N, 13.59. Found: C, 65.81; H, 5.19; N, 13.64

3-CH$_3$-py-2-NHCH$_2$PPh$_2$ (3): AlH_3-THF (1.48 mL, 0.55 M) was added slowly to stirred solution of **1** (0.250 g, 0.78 mmol) in dry-THF (5 mL). The mixture was refluxed for 1 h and

reaction was monitored by ^{31}P-NMR spectroscopy. After the reduction was complete, the mixture was cooled to room temperature and methanol (95 μL, 2.33 mmol) was added. The slurry was filtered over celite and washed with hot dry-THF (3 × 5 mL). The volatiles in filtrate were removed under reduced pressure, and the oily product was obtained (0.200 g). Yield: (84%). **3.** ^{31}P NMR (162 MHz, $CDCl_3$) δ -16.7 (s).

pyz-2-NHCH$_2$PPh$_2$ (4): This compound was prepared by the same procedure for **3** given above and obtained as colorless oil (0.225 g). Yield: 88%. ^{31}P NMR (162 MHz, $CDCl_3$) δ -17.0 (s).

(3-CH$_3$-py-2-NHCH$_2$PPh$_2$)$_2$PdCl$_2$ (5): Pd(COD)Cl_2 (0.043 g, 0.15 mmol) in CH_2Cl_2 (5 mL) was added to a solution of **3** (0.094 g, 0.31 mmol) in CH_2Cl_2 (20 mL) and then stirred at room temperature for 30 min. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, and diethyl ether was added to precipitate the product. The resulting light yellow solid was filtered and then dried. Yield: 0.102 g (86%). IR : 3327 cm^{-1} (νNH), 327 and 285 cm^{-1} (νPd-Cl) . ^{1}H NMR (400 MHz,) δ 8.04 (s, 2H), 7.53 – 7.29 (m, 20H), 7.17 (s, 2H), 6.54 (s, 2H), 5.69 (s, 2H), 4.46 (s, 4H), 1.90 (s, 6H). ^{13}C NMR (101 MHz,) δ 156.6 (d, *J* = 3.6 Hz), 145.4 (s), 136.8 (s), 133.9 (d, *J* = 94.4 Hz), 133.0 (d, *J* = 18.3 Hz), 129.0 (d, *J* = 6.6 Hz), 128.7 (d, *J* = 6.6 Hz), 116.9 (s), 113.03 (s), 39.9 (d, *J* = 69.4 Hz), 16.6 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.5 (s). Anal. Calcd for $C_{38}H_{38}Cl_2N_4P_2Pd$: C, 57.77; H, 4.85; Cl, 8.98; N, 7.09; P, 7.84; Pd, 13.47. Found: C, 58.06 H, 4.87; N, 7.12.

(Pyz-2-NHCH$_2$PPh$_2$)$_2$PdCl$_2$ (6): This compound was prepared by the same procedure for **5** given above and obtained as light yellow solid. Yield : 0.082 g (63%). IR : 3353 cm^{-1} (νNH), 319 and 284 cm^{-1} (νPd-Cl). ^{1}H NMR (400 MHz,) δ 8.07 (s, 2H), 7.90 (d, *J* = 0.8 Hz, 2H), 7.83 – 7.75 (m, 4H), 7.73 (d, *J* = 2.7 Hz, 2H), 7.56 – 7.40 (m, 6H), 5.22 (s, 2H), 4.31 (s, 4H). ^{13}C NMR

(101 MHz,) δ 154.2 (d, *J* = 5.8 Hz), 141.1 (s), 132.5 (d, *J* = 104.2 Hz), 132.3 (d, *J* = 1.9 Hz), 131.4 (s), 131.1 (d, *J* = 9.5 Hz), 130.4 (s), 128.8 (d, *J* = 11.7 Hz), 40.3 (d, *J* = 65.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.5 (s). Anal. Calcd for $C_{34}H_{32}Cl_2N_6P_2Pd$: C, 53.46; H, 4.22; Cl, 9.28; N, 11.00; P, 8.11; Pd, 13.93. Found: C, 53.25; H, 4.24; N, 10.96.

General procedure for Heck cross-coupling reaction

Heck coupling reactions were carried out in air. In a typical experiment, an oven-dried, sealed tube equipped with a magnetic stir bar was charged with aryl bromide (0.1 mmol), styrene (0.12 mmol) and a base (0.12 mmol). The catalyst solution (0.0004 mmol catalyst in 2.0 ml solvent) was then added. The reaction mixture was placed in a silicon oil bath at 140 °C and stirred. After the required reaction time, the mixture was allowed to cool to room temperature, diluted with CH_2Cl_2, and washed with HCl aqueous solution and brine. The organic phase was separated and dried over Na_2SO_4, and the solvent was evaporated. The residue was chromatographed on silica gel using an ethyl acetate/hexane (1:5) mixture as eluent. Conversion percentages were determined from the solution by GC analysis, and isolated yields, which were characterized by ^{1}H and ^{13}C NMR, determined by GC based on ArBr.

Computational Method

Numerical calculations were achieved by using GaussView 5.0.8[18] and Gaussian 09 AM64L-G09RevD.01[19]. Becke,3-parameter,Lee-Yang-Parr (B3LYP) method[20,21] was selected as computational method for studied complexes. LANL2DZ and 6-31G(d) basis sets were used in complex calculations for metal atoms and rest atoms in complex, respectively. All calculations

were made in gas phase. Imaginary frequency was not obtained in whole calculations. According to Koopmans theorem, the HOMO and LUMO energies were associated with Eqs. (1) and (2):

$$I = -E_{HOMO} \quad (1)$$

$$A = -E_{LUMO} \quad (2)$$

Some quantum chemical parameters which are E_{GAP}, η, σ, χ, ω and N were calculated by using Eqs. (3)-(8)[19,22-25]

$$E_{GAP} = E_{LUMO} - E_{HOMO} \quad (3)$$

$$\eta = \frac{I - A}{2} \quad (4)$$

$$\sigma = \frac{1}{\eta} \quad (5)$$

$$\chi = \frac{|I + A|}{2} \quad (6)$$

$$\omega = \frac{\chi^2}{2\eta} \quad (7)$$

$$N = \frac{1}{\omega} \quad (8)$$

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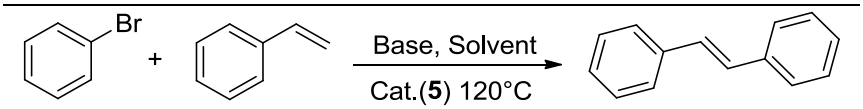
Table 1. The results of optimization experiments of Heck reaction.[a, b]

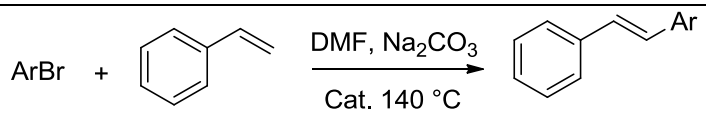


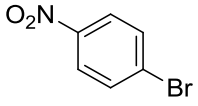
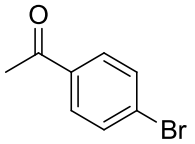
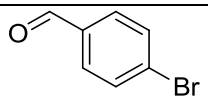
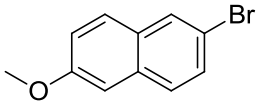
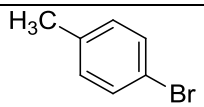
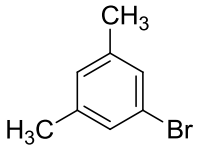
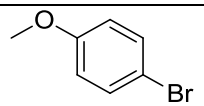
Entry	Base	Solvent	T (°C)	Conversion (%)
1	Na_2CO_3	DMF	140	92
2	K_2CO_3	DMF	140	38
3	NaOAc	DMF	140	77
4	NEt_3	DMF	140	18
5	Na_2CO_3	1,4-Dioxane	140	< 5
6	K_2CO_3	1,4-Dioxane	140	< 5
7	NaOAc	1,4-Dioxane	140	13
8	NEt_3	1,4-Dioxane	140	< 5

[a] Conditions : Bromobenzene (0.1 mmol), stryrene (0.12 mmol), Base (0.12 mmol), catalyst (0,0004 mmol), solvent (2.0 mL)

[b] Percentage conversions were determined by GC based on bromobenzene after 3 h.

Table 2. Results of Heck cross-coupling reaction of styrene with aryl bromides.[a]

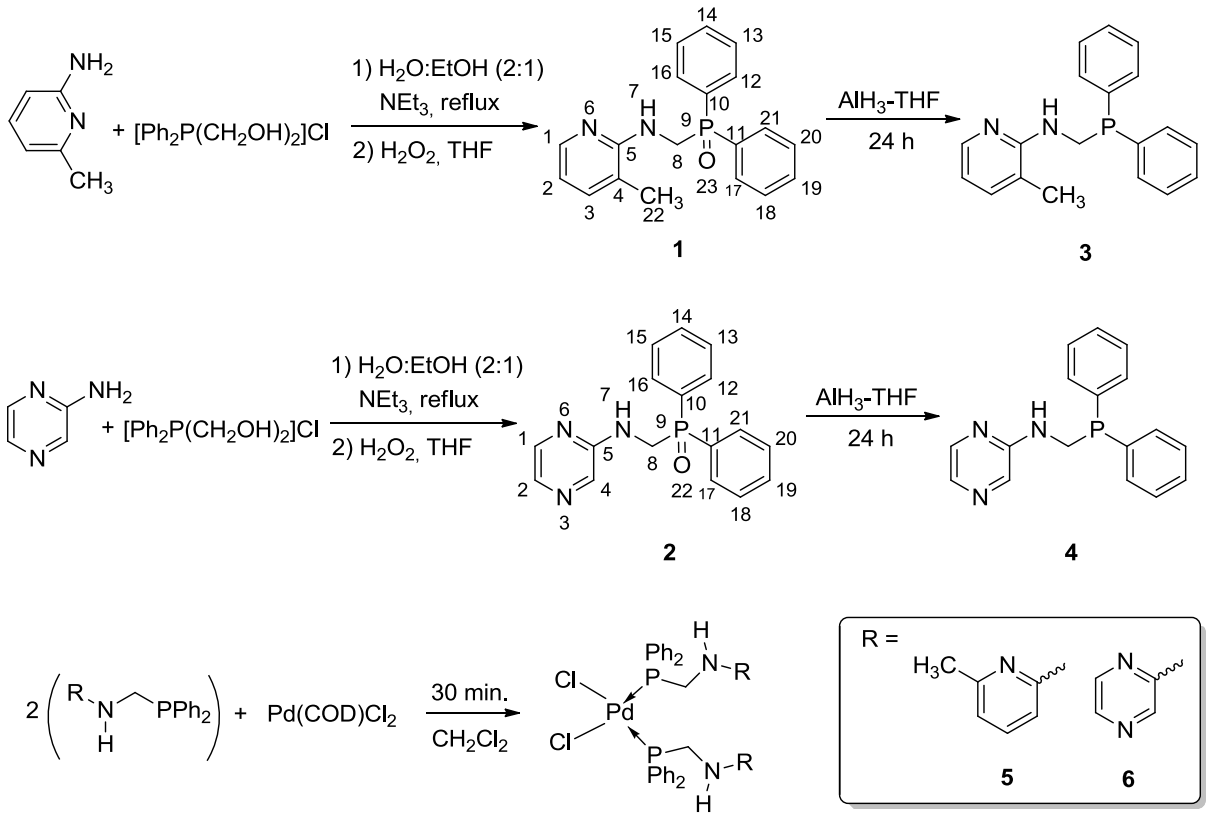


Entry	ArBr	Cat.	Time (h)	Conversion[b] (%)	Yield[c] (%)
1		**5**	3	100	82
		6	8	100	85
2		**5**	3	100	91
		6	8	100	93
3		**5**	3	100	93
		6	8	100	92
4		**5**	3	96	87
		6	8	78	78
5		**5**	8	85	78
		6	8	88	81
6		**5**	8	78	73
		6	8	81	75
7		**5**	8	94	86
		6	8	89	78

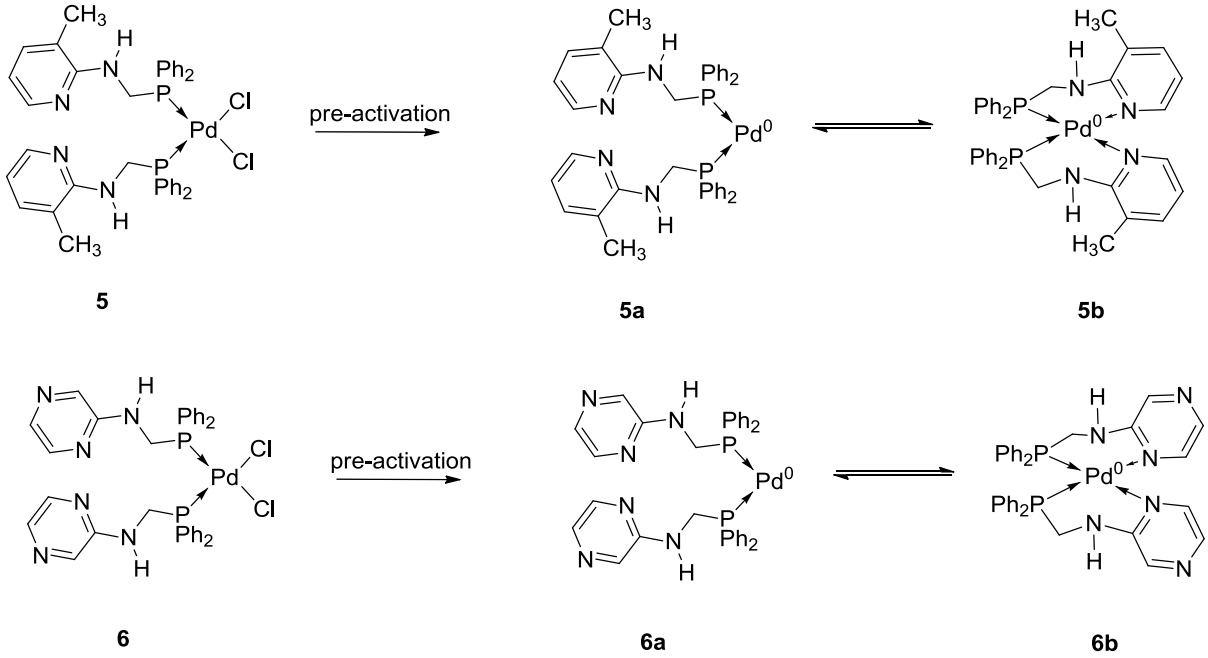
[a] Conditions : ArBr (0.1 mmol), stryrene (0.12 mmol), Na_2CO_3 (0.12 mmol), catalyst (0.0004 mmol), DMF (2.0 mL)

[b] Percentage conversions were determined by GC based on ArBr.

[c] Isolated yields, which were characterized by ^{1}H and ^{13}C NMR, determined by GC based on ArBr



Scheme 1. Synthetic route of ligands and metal complexes



Scheme 2. Supposed structures occurred after the pre-activation step.