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Graphical Abstract

Crystal structure of a new polymorph of trans-dichlorobis (triphenylphosphine) palladium (II) and its application as a novel, efficient and retrievable catalyst for the amination and Stille cross-coupling reactions

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Crystal structure of a novel polymorph of trans-dichlorobis (triphenylphosphine) palladium (II) and its application as a novel, efficient and retrievable catalyst for the amination of aryl halides and Stille cross-coupling reactions

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Abstract:

In this study, synthesis, characterization and X-ray crystal structural characterization of trans [PdCl₂(PPh₃)₂] complex are described. This compound has been fully characterized by elemental analysis (CHN), FT-IR, ¹H, ¹³C and ³¹P-NMR and also X-ray crystallographic. In this structure, the geometry around palladium atom is a slightly distorted square-planar. It was found that this compound can act as an efficient catalyst for amination of aryl halides to afford primary amines and has also been successfully employed in the catalytic stille cross-coupling reaction with satisfactory results. The catalyst showed recyclability and it can be reused without essentially losing its catalytic activity frequently.

Keywords: Phosphonium; Palladium(II) Chloride; X-ray crystal; Amination; Stille cross-coupling.

1. Introduction

Synthetic chemists' arylation of amines using Palladium as a catalyzer is a powerful technique which serves as a useful tool for them in the synthesis of essential intermediates. It is also widely used as an integral part of photographic materials, pharmaceuticals, conducting polymers and fine chemicals [1-4]. Topics which still attract researchers' attention in the field of designing new ligands are improving the scope of substrate as well as efficiency [5,6]. A significant contribution in this regard, comes from large phosphine ligands rich in electrons [7,8] and carbine ligands which are N-heterocyclic [9-11]. Such ligands facilitate Pd-catalyzed aminations to a great extent. Yet, these ligands are not easily synthetized due to the high cost of materials used and the cumbersome procedure applied. So, there seems to be a need for more easily available and cheaper systems of catalysis to be adopted in industry [12].

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An inexpensive and readily accessible phosphine that has been widely used in Pd-catalyzed coupling reactions is Triphenylphosphine (Ph_3P). But the problem is that this phosphine is not considered as effective when applied to intermolecular amination reactions, perhaps because its steric hindrance is smaller and it is not as rich in electrons [13-15]. Despite this, researchers are still interested in Ph_3P due to its low cost, air stability and commercial accessibility [16].

In this paper, we report the synthesis, characterization and crystal structure determination a novel triclinic polymorph of the Trans-dichlorobis (triphenylphosphine) palladium (II) complex with two independent molecules. Accordingly, as a part of our ongoing attempt to examine this phenomenon in molecular crystals, we have also investigated polymorphism in transition metal complexes. Based on our knowledge, this complex has not been examined for the amination of aryl halides with aqueous ammonia. Therefore, to extend our previous work as to catalytic reactions [17,18], to obtain primary amines, aqueous ammonia is applied successfully as a green direct nitrogen source under air atmosphere and solvent free conditions. Thus, we report the catalytic activity of this trans-dichlorobis (triphenylphosphine) palladium (II) compound for C-C bond formation by the Stille cross-coupling reaction using triphenyltin chloride under green medium to obtain biphenyl derivatives. Biphenyl derivatives have wide range of activities, including anti-diabetic, antimicrobial, anti-proliferative, antifungal, anti-inflammatory, immunosuppressant, etc. [19-21].

2. Experimental

2.1. Materials and physical measurements

All reactants and solvents were obtained from Merck and Aldrich Chemical Companies and used without further purification. Melting points were measured on a Stuart SMP₃ apparatus. IR spectra in the range 4000-400 cm⁻¹ were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. NMR spectra (¹H, ¹³C and ³¹P- NMR) recorded on a 400 MHz Bruker spectrometer in CDCl₃ as the solvent at room temperature. Elemental analysis was carried out with a CHNS-O Costech ECS 4010 analyzer. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by a UV fluorescence lamp.

2.2. X-ray crystallography

The single crystal X-ray diffraction data of suitable crystals was collected on a STOE IPDS-II diffractometer at 120(2) K, using graphite monochromated Mo Ka radiation (0. 0.71073 Å). The data collection was performed using the ω -scan technique and using the STOE X-AREA software package [22], whereas data diminution was carried out using the program X-RED [23]. The structure was solved by direct methods and subsequent difference Fourier maps and then refined on F² by full-matrix least-squares procedures using the programs SHELX and SHELXL respectively [24], and all refinements were performed using the XSTEP32 crystallographic software package [25]. All hydrogen atoms were added in geometrically idealized positions.

2.3. Synthesis of trans-dichlorobis (triphenylphosphine) palladium (II)

Palladium(II) chloride (0.088 g, 0.50 mmol) and sodium chloride (0.0876 g, 1.50 mmol) were dissolved in methanol (15 ml). Then, n-methyl benzylamine (0.121 gr, 1.0 mmol) was added to the solution and the mixture was stirred at room temperature for 12 h. The separated solid was filtered off and washed with diethyl ether to give $[Pd{CH_2NHCH_3(C_6H_4)(\mu-Cl)}]_2$ (1) as a yellow powder. Yield: 0.147 g (87%).

To a solution of the compound $[Pd{CH_2NHCH_3(C_6H_4)(\mu-Cl)}]_2$ (0.521g, 1 mmol) in dichloromethane (15 mL), triphenylphosphine (0.524 g, 2 mmol) was added, and the resulting solution was stirred at room temperature for 6 h. The suspension that formed was filtered off, washed with diethyl ether and dried to give trans- $[PdCl_2(PPh_3)_2]$ (2) as an yellow powder. Yield: 0.057 g (92%), m.p: 170 °C. Anal. Calc. for $C_{36}H_{30}Cl_2PPd$ (701.84 g/mol): C, 61.60; H, 4.31. Found: C, 60.96; H, 4.11%. IR (KBr disk, ϑ cm⁻¹): 1485-1587 (C=C), 670-850 (C-H in Ph), 1435 (P-C). ¹H NMR (400 MHz, CDCl₃, ppm) δ : 7.11–7.76 (m, 30H, Ph). ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 128.04, 130.12, 131.44, 134.01 (m, Ph). ³¹P{¹H} NMR (162 MHz, CDCl₃, ppm) δ : 23.28 (s, PPh₃).

2.4. General procedure for amination of aryl halides

To a solution of the aryl halide (1 mmol), ammonium hydroxide (28%) (1 mL, 0.003 mmol), Na_2CO_3 (1.5 mmol) and 0.010 g (0.014 mmol) of trans-[PdCl₂(PPh₃)₂] as a catalyst were added and the reaction mixture was stirred at 80 °C for an appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the product was extracted with ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous MgSO₄, filtered and evaporated to give the pure product. The products were characterized by comparing their spectral and physical data with those of the credible samples.

2.5. General procedure for the Stille cross-coupling reaction

A mixture of the aryl halide (1 mmol), triphenyltin chloride (0.5 mmol), Na₂CO₃ (1.5 mmol), 0.007 g (0.001 mmol) of trans-[PdCl₂(PPh₃)₂] as a catalyst and 2 mL polyethylene glycol (PEG) as the solvent was heated at 90 °C and the progress of the reaction was monitored by TLC. After cooling the reaction mixture, the reaction mixture was added to water, filtered (to remove the catalyst) and extracted three times with diethyl ether. The organic layer was dried over MgSO₄ and the solvent was evaporated. The products were characterized by comparing their spectral and physical data with those of the credible samples.

2.6. Selected Spectral data

4-Nitroaniline (Table 4, entry 9): ¹H NMR (400 MHz, CDCl₃. ppm): $\delta = 8.08-8.12$ (d, J=9.3 Hz, 2H); 6.65-6.67 (d, J= 8.8 Hz, 2H); 4.43 (br, 2H). IR (ν , cm⁻¹): 3419, 3391, 3096, 3060, 2958, 2927, 2856, 1921, 1732, 1603, 1568, 1517, 1474, 1436, 1397, 1354, 1345, 1308, 1278, 1173, 1122, 1106, 1067, 1013, 958, 855, 839, 738, 725, 693, 678, 623, 544, 522.

4-Cyanoaniline (Table 4, entry 10): ¹H NMR (400 MHz, CDCl₃. ppm): $\delta = 7.67-7.69$ (m, 2H); 7.54-7.58 (m, 2H); 4.28 (br, 2H). IR (ν , cm⁻¹): 3087, 3035, 2966, 2929, 2863, 2286, 2224, 1916, 1725, 1657, 1584, 1475, 1397, 1277, 1176, 1124, 1068, 1013, 962, 826, 769, 748, 724, 696, 545, 433.

[1,1'-biphenyl]-4-carbonitrile (Table 6, entry 6): ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.76-7.79 (m, 2H); 7.69-7.72 (m, 2H); 7.64 -7.66 (m, 2H); 7.52-7.56 (m, 2H); 7.46-7.48 (m, 1H). IR (ν , cm⁻¹): 3432, 3065, 2923, 2351, 2216, 1927, 1638, 1596, 1475, 1398, 1275, 1108, 953, 844, 767, 692, 558, 511.

4-Nitro-1,1'-biphenyl (Table 6, entry 9): ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 8.34$ (d, J= 8.7 Hz, 2H , 2H); 7.78 (d, J= 8.9 Hz, 2H); 7.64-7.67 (m, 2H); 7.52-7.56 (m, 2H); 7.47-7.52 (m, 1H). IR (ν , cm⁻¹): 3445, 3074, 2926, 2842, 1923, 1674, 1591, 1513, 1399, 1343, 1105, 926, 854, 738, 691, 534, 468.

3. Results and discussion

3.1. Catalyst characterization

This palladium dimmer complex was easily synthesized by reaction of sodium chloride with Palladium (II) chloride and N-methyl benzylamine in a molar ratio of 3:1:2 in methanol at room temperature for 12 h. The resulting suspension was filtered off and the obtained precipitate was washed with diethyl either and then methanol, and subsequently dried to give the related $[Pd{CH_2NHCH_3(C_6H_4)(\mu-Cl)}]_2$ (1) as yellow powder. Dichloromethane with ligand triphenylphosphine was added to a solution of compound 1, resulting in the immediate precipitation of NaCl. This solution further stirred for 6 h at room temperature and then filtered. The clear yellow solution was evaporated and residue treated with diethyl ether to give a yellow solid of complex 2. Scheme 1 shows the procedure for preparing the so called compound.

Scheme 1 here

Compound is a coordination compound of palladium containing two triphenylphosphine and two chloride ligands. As mentioned in experimental and also in scheme 1, these reactions led to the easy synthesis of the palladium phosphine complex. The observed sharp and singlet peak at δ = 23.28 ppm by ³¹P NMR confirmed the purity of the product. Eventually, the structure was

established by single crystal X-ray diffraction study. We report here a new triclinic polymorph of the asymmetric unit of the title compound, $C_{36}H_{30}Cl_2P_2Pd$, contains two independent molecules (molecule 1 and molecule 2, Fig. 1). The molecular structure of complex was determined by X-ray diffraction. Yellow crystals of complex **2** were obtained from a methanol /chloroform solution by slow evaporation of the solvent over several days and its structure was determined by single-crystal X-ray diffraction. The title compound, trans-[PdCl₂(PPh₃)₂], has a slightly distorted square-planar geometry, with the chloride ligands coordinated in a Trans configuration. Table 1 provides the crystallographic result and parameters concerning data, structure solution and refinement information for complex. Tables 2, show the selected bond lengths and angles for complex (II).

Figure 1 here

Table 1 here

Table 2 here

3.2. Catalytic study

The activity of the described catalyst was investigated through a reaction of aryl halides with aqueous ammonia and triphenyltin chloride for the synthesis of aniline and biphenyl derivatives, respectively. Initially, we examined the reaction of iodobenzene with aqueous ammonia in different solvents, bases, temperature and various catalytic amounts of trans-[PdCl₂(PPh₃)₂]. The results are shown in Table 3. For this reaction, different amounts of catalyst between 5 and 15 mg were further examined, moreover, 10 mg catalyst was found to be optimal (Table 3, entry 11). In addition, the desired product was obtained in a nearly quantitative yield for the higher amounts of catalyst (Table 3, entry 12). Our next studies focused on the influence of solvent in the model reaction. The comparison of the results demonstrated that the reaction in the presence of NH₃.H₂O as solvent proceeded much better than other solvents with a good yield in short reaction time (Table 3, entry 4). After selecting NH₃.H₂O as the optimal solvent, we examined the influence of various bases on aqueous ammonia. In the presence of Na₂CO₃, NaOAc, KHCO₃ and Et₃N bases, the yield of 82 %, 72 %, 65 % and 78 % were obtained, respectively (Table 3, entries 4-7). It has been proved that Na_2CO_3 was the most efficient and gave the good isolated yield (Table 3, entry 4). The reaction was promoted significantly by increasing the temperature from 60 to 80 °C (Table 3, entry 4 and 9). For activated aryl halides, the reaction was conveniently carried out at 80 °C. However, a higher temperature at about 100 °C is required for activation of bromobenzene. Incomplete conversion of the starting materials is often resulted by lowering the temperature (Table 3, entry 10).

Table 3 here

Optimal conditions for the reaction were determined as follows: 1 mmol of iodobenzene, 1 mL of aqueous ammonia, 1.5 mmol of Na_2CO_3 as base and 0.001 g of catalyst in at 80 °C (Table 3, entry 4). The coupling reaction proceeds easily with aryl bromides and iodides with aqueous ammonia after optimizing the reaction conditions. The results have been summarized in Table 4. As shown in Table 4, in order to afford the corresponding anilines with good yields, all of the examined aryl halides such as bromides and iodides reacted with aqueous ammonia.

Table 4 here

After successful synthesis of a wide range of aniline in good yields, we explored the use of the so called catalytic system for the synthesis of biphenyl derivatives from aryl halides and triphenyltin chloride. In our preliminary experiments, the reaction between iodobenzene and triphenyltin chloride was examined to optimize the reaction conditions such as solvent, base, catalyst amount and temperature. The results are summarized in Table 5. At first, we found that the reaction did not proceed in the absence of trans- $[PdCl_2(PPh_3)_2]$ (Table 5, entry1). Then, the optimum temperature for the reaction was 90 °C based on the variation of temperature in the range 25-90 °C. In the case of 70 °C, the yield of the desired product was lower than the one at 90 °C (Table 5, entries 3 and 6). However, the yield of the desired product did not increase obviously when the temperature increased to 110 °C (Table5, entry 7). Optimizing the conditions so as to select the best solvent from the commonly used ones was the next step. Among the tested solvents, DMSO and DMF led to corresponding biphenyl product in 82 % and 75 % yields (Table5, entries 8 and 9) in the presence of 5 mg of trans-[PdCl₂(PPh₃)₂]. While in solvents such as H₂O and EtOH, trace amounts of product were obtained (Table 5, entries 10 and 11). The product was isolated 94 % yield in the case of PEG-400 solvent (Table 5, entry 6). The results demonstrated that PEG-400 was the best solvent for the reaction. Our next studies paid attention to the influence of base in the model reaction. Among the bases tested, it appeared that Na₂CO₃ act as an excellent base for this reaction (Table 5, entry 6). Organic bases including KHCO₃, NaOAc and Et₃N were substantially less effective (Table 5, entries 12 -14).

Table 5 here

The generality of this reaction was investigated using several types of various aryl halides, such as chlorides, bromides and iodides, having electron donating and electron withdrawing groups. The results have been summarized in Table 6. As shown in Table 6, all of the examined aryl iodides and bromides reacted with triphenyltin chloride in good yields but the ideal substrates are aryl bromides and iodides since aryl chlorides are generally less reactive resulting in longer reaction time and lower conversion.

Table 6 here

3.3. Reusability of the catalyst

Reusability is an advantage of catalysts that makes them significant from a commercial point of view. Therefore, the recyclability of the catalyst was investigated for the reaction of iodobenzene with aqueous ammonia and triphenyltin chloride under the optimal conditions. After completion of the reaction based on TLC, the reaction mixture was cooled to room temperature. Then water and the organic phase of the reaction, ethyl acetate in the amination reaction or diethyl ether in the Stille reaction, were added and the mixture was filtered off to separate the catalyst. The catalyst was dried at 120 °C and directly used for the repeated reactions. As shown in Figure 2, the heterogeneous catalyst can be recycled up to four consecutive runs in the amination reaction and synthesis of biaryl compounds without any significant loss of its catalytic activity.

Figure 2 here

4. Conclusion

We used palladium complex 2 containing two triphenyl phosphine ligands as an efficient and well defined catalyst for the amination and biphenyl reactions of various aryl halides. This complex is highly active and efficient catalyst for promoting the amination and Stille cross-coupling reactions of various aryl halides to produce the corresponding products in moderate to excellent yields. The performance of amination reaction under solvent-free condition makes this synthetic strategy fascinating from the environmental perspective. Also the catalyst can be reused for 4 times without essentially losing its catalytic activity frequently. The facility of catalyst precursors' preparation, low catalyst loading, its high solubility in organic solvents and stability toward air make the complex ideal starting material for the above transformations.

Appendix A. Supplementary data

CCDC No. 965011 contains the Supplementary crystallographic data for the compound. These data can be obtained free of charge via <u>http://www.ccdc.ac.uk/conts/retriving.html</u>, or from the Cambridge crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: <u>deposit@ccdc.cam.ac.uk</u>

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Scheme 1 Synthesis of trans-dichlorobis (triphenylphosphine) palladium(II).



Fig 1 X-Ray structure of trans-dichlorobis(triphenylphosphine) palladium(II).



Fig. 2 Reuse of the catalyst in Aniline and Stille cross-coupling reactions.

Identification code	[(C ₆ H ₅) ₃ P] ₂ PdCl ₂
Empirical formula	$C_{36}H_{30}Cl_2P_2Pd$
Formula weight	701.84
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	9.1193 (18)
b (Å)	9.6487 (19)
c (Å)	29.379 (6)
α(°)	84.12 (3)
β (°)	89.23 (3)
γ(°)	67.79 (3)
Volume (Å ³)	2379.8 (10)
Z	3
Calculated density, Mg/m ³	1.469
F(000)	1068
Theta range for data collection, (°)	2.41 to 29.16
Limiting indices	$-12 \le h \le 12, -13 \le k \le 13, -40 \le 1 \le 35$
Completeness to theta $= 29.160$	98.2 %
Absorption correction	Numerical
Absorption coefficient (mm ⁻¹)	0.879
Crystal size (mm ³)	$0.32 \times 0.12 \times 0.10$
Reflections collected/ unique	25496/12639 [<i>R</i> (int) = 0.0856]
Max. and min. transmission	0.9173 and 0.7663
Refinement method	Full-matrix least-squares on F ²
Data/restraints/ parameters	12639/30/544
Goodness-of-fit on F ²	1.019
Final R indices [I>2 δ (I)]	$R_1 = 0.0588, WR_2 = 0.0901$
R indices (all data)	$R_1 = 0.1074, WR_2 = 0.1020$
Largest diff. peak and hole, e Å ⁻³	0.88 and -0.87

Table 1 Crystal data and structure refinement for compound 2.

	U		1
B	ond Lengths	Bond	Angles
Pd(1)-Cl(1)	2.2954(14)	Cl(2)-Pd(1)-Cl(1)	179.61(5)
Pd(1)-Cl(2)	2.2940(14)	Cl(2)-Pd(1)-P(2)	88.13(5)
Pd(1)-P(2)	2.3355(13)	Cl(1)-Pd(1)-P(2)	91.51(5)
Pd(1)-P(1)	2.3363(13)	Cl(2)-Pd(1)-P(1)	92.14(5)
Pd(2)-Cl(3)	2.2923(15)	Cl(1)-Pd(1)-P(1)	88.23(5)
Pd(2)-P(3)	2.3389(12)	P(2)-Pd(1)-P(1)	177.29(4)
P(1)-C(1)	1.819(5)	Cl(3)-Pd(2)-Cl(3)	180.00(6)
P(1)-C(7)	1.822(4)	Cl(3)-Pd(2)-P(3)	88.43(5)
P(1)-C(13)	1.817(5)	Cl(3)-Pd(2)-P(3)	91.57(5)
P(2)-C(19)	1.827(4)	P(3)-Pd(1)-P(3)	180.00(3)
P(2)-C(25)	1.814(4)	C(13)-P(1)-Pd(1)	112.53(14)
P(2)-C(31)	1.821(4)	C(1)-P(1)-Pd(1)	118.00(16)
P(3)-C(37)	1.820(5)	C(7)-P(1)-Pd(1)	110.11(14)
P(3)-C(43)	1.826(5)	C(49)-P(3)-Pd(2)	112.03(16)
P(3)-C(49)	1.815(4)	C(43)-P(3)-Pd(2)	118.13(19)
C(1)-C(6)	1.391(7)	C(37)-P(3)-Pd(2)	111.34(16)

Table 2 Selected bond lengths (A°) and bond angles $(^{\circ})$ for compound 2.

Table 3 Optimization of various parameters for the amination of iodobenzene with NH₄OH.

	I		trans-[PdCl ₂ (PPh ₃) ₂] (Cat.)			\sim NH ₂
		+ NH ₄ OH	Solvent, Base, temperture			
Entry	Cat (mg)	Solvent	Base	Temp (°C)	Time (h)	Yield (%) ^a
1	5	DMF	Na ₂ CO ₃	60	7	44
2	5	EtOH	Na ₂ CO ₃	60	7	58
3	5	H ₂ O	Na ₂ CO ₃	60	7	65
4	5	NH ₃ .H ₂ O	Na ₂ CO ₃	60	7	82
5	5	NH ₃ .H ₂ O	NaOAC	60	7	72
6	5	NH ₃ .H ₂ O	KHCO ₃	60	7	65
7	5	NH ₃ .H ₂ O	Et_3N	60	7	78
8	5	NH ₃ .H ₂ O	Na ₂ CO ₃	r.t	7	
9	5	NH ₃ .H ₂ O	Na ₂ CO ₃	80	7	86
10	5	NH ₃ .H ₂ O	Na ₂ CO ₃	100	7	87
11	10	NH ₃ .H ₂ O	Na ₂ CO ₃	80	7	92
12	15	NH ₃ .H ₂ O	Na ₂ CO ₃	80	7	93

^a Isolated yield.

		$MH_4OH = \frac{trans - [PdCl_2(I)]}{2}$	$PPh_3)_2]$ (Cat.)		NH ₂
	R	Solvent free, f	$Na_2CO_3, 80$ °C	R	
Entry	Aryl halide	product	Time (h)	Yield (%) ^b	M.P. (° C)
1	I	NH ₂	7	92	yellow oil ^[26]
2	Br	NH ₂	12	89	yellow oil ^[26]
3	Me	Me NH ₂	10	90	42-45 [27]
4	Me	Me NH ₂	13	87	42-45 [27]
5	MeO	MeO NH ₂	8	91	57-59 ^[27]
6	MeO	MeO NH ₂	10	88	57-59 ^[26]
7	OHC	OHC NH ₂	6	90	69–71 ^[26]
8	Br H ₂ N	H ₂ N NH ₂	7	93	135-137 [26]
9	O ₂ N Br	O ₂ N NH ₂	5	92	147-149 [27]
10	NC	NC NH ₂	8	90	84-86 [28]

Table 4 Preparation of aniline derivatives from aryl halides in the presence of catalytic.^a

^aReaction conditions: 1 mmol of aryl halide, 1 mmol of aqueous ammonia, 1.5 mmol of Na₂CO₃, and 0.01 g of catalyst at 80 °C. ^bIsolated yield.

	I	Ph ₃ SnCl	trans-[Pd	$[Cl_2(PPh_3)_2]$ (C	Cat.)	Ph	
	+	5	Solvent, Base, temperture				
Entry	Cat (mg)	Solvent	Base	Temp (°C)	Time (min)	Yield (%) ^a	
1		PEG	Na ₂ CO ₃	70	120		
2	5	PEG	Na ₂ CO ₃	70	120	83	
3	7	PEG	Na ₂ CO ₃	70	25	88	
4	10	PEG	Na ₂ CO ₃	70	20	89	
5	7	PEG	Na ₂ CO ₃	r.t.	25		
6	7	PEG	Na ₂ CO ₃	90	25	94	
7	7	PEG	Na ₂ CO ₃	110	25	95	
8	7	DMSO	Na ₂ CO ₃	90	25	82	
9	7	DMF	Na ₂ CO ₃	90	25	75	
10	7	EtOH	Na ₂ CO ₃	90	25	42	
11	7	H_2O	Na ₂ CO ₃	90	25	38	
12	7	PEG	NaOAC	90	25	85	
13	7	PEG	KHCO ₃	90	25	81	
14	7	PEG	Et ₃ N	90	25	91	

Table 5 The optimization of reaction parameters for the Stille cross-coupling reaction of iodobenzene with Ph_3SnCl .

^aIsolated yield.

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	I + Ph ₃ SnC	trans-[PdCl	$_2(PPh_3)_2]$ (Cat.		~Ph
	R	PEG, Na ₂	CO ₃ , 90 °C	R	~
Entry	Aryl halide	Product	Time (min)	Yield (%) ^b	Mp (°C)
1	I	Ph	25	94	68 ^[29]
2	Br	Ph	35	91	68 ^[29]
3	Cl	Ph	50	88	68 ^[29]
4	H ₃ C H	Ph	30	90	45-47 [26]
5	H ₃ C H	Ph BC	25	88	45-47 [26]
6	NC	NC Ph	30	90	84-86 [30]
7	NC	NC Ph	65	84	84-87 [26]
8	Cl	Ph	45	85	76-77 [30]
9	O ₂ N O	Ph	25	92	111-113 [26]
10	O ₂ N O	Ph	55	86	111-113 [31]
11	H ₃ CO H ₃ C	Ph	35	88	83-85 ^[26]
12	H ₃ CO H ₃ C	Ph	40	87	83-85 [26]

Table 6 Stille cross-coupling for the synthesis of biaryls from aryl halides.^a

^aReaction conditions: 1 mmol of aryl halide,0.5 mmol of Ph₃SnCl, 1.5 mmol of Na₂CO₃, and 0.007 g of catalyst in 2 mL of PEG solvent at 90 $^{\circ}$ C.

^bIsolated yield.

Highlights:

- 1. trans $[PdCl_2(PPh_3)_2]$ complex was prepared
- 2. trans [PdCl₂(PPh₃)₂] complex characterized by X-Ray crystallography
- 3. trans [PdCl₂(PPh₃)₂] complex catalyzed amination and C-C coupling reaction