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Synthesis of novel tridentate ligand-based palladium catalyst and investigation of its reactivity towards Suzuki, Sonogashira and Heck coupling reactions

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ABSTRACT

We have demonstrated a simple and efficient route for the synthesis of a novel imine based tridentate ligand and its Pd-complex to investigate the C-C cross-coupling reactions, that involve column chromatography purification in only one step. The catalytic activity of the newly synthesized catalyst was studied for the Suzuki, Sonogashira and, Heck cross-coupling reactions under mild conditions. All synthesized molecules are thoroughly characterized by IR and NMR techniques. The pro-ligand was characterized by a single Crystal X-ray diffraction study. The catalyst has excellent activity and good yield was obtained with minimum catalyst loading. The obtained yields are good to excellent.

***Keywords**: C-C Cross coupling, Pd complex, Tridentate ligand, Palladacycle.*

1. Introduction

Metal catalyzed C-C bond formation between two sp^2 carbons is very interesting as many molecules of biological importance [1,2], polymers [3,4], pesticides [5], OLED [6], and solar cell energy harvesting materials [7,8] can be easily obtained from simple and readily available coupling partners. Exhaustive research on Pd catalyzed coupling reactions such as Suzuki [9,10], Heck [11,12], Sonogashira [13,14], Negishi [15,16], etc. has overcome the most of the practical difficulties and drawbacks encountered in the initially developed reaction condition. Despite a few drawbacks such as the toxicity of palladium, the cost of the catalyst, less or non-reactivity of aryl chlorides to undergo oxidative addition, Pd-catalyzed coupling has been identified as the most promising reaction for the coupling of sp^2 hybridized carbon with another sp^2 carbon or sp carbon under mild conditions [17,18]. In order to find more commercial applications for these reactions, several modifications have been attempted varying solvents, reusable heterogeneous catalyst and the substrate.

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More focus is given to the catalyst as it is expensive, toxic and the reactivity of the catalyst can be fine-tuned by changing the ligands. Several phosphine ligands such as BINAP [19,20], PPh_3 [21], JohnPhos [22, 23], XantPhos [24, 25], etc. have been reported to promote the reactivity. Nitrogen based ligands are also employed often in the form of palladacycle (**Fig**.**1**) [26-30].

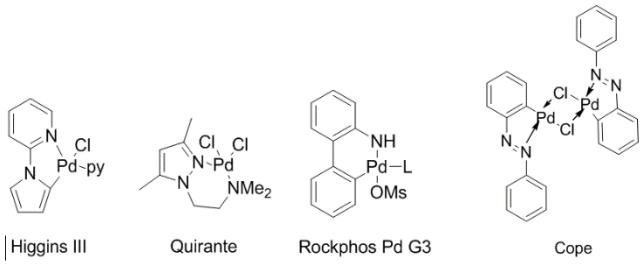


Fig. 1. Structure of Palladacycles

Even though most of the major problems have been solved, the search for more efficient and cheaper ligand has still possibility and several research groups are continuously working to develop a novel ligand for metal catalysts. In this communication we report a new, simple and high yielding synthesis of an imine based tridentate ligand, its complex with palladium and investigation of the efficiency of catalyst towards Suzuki, Heck and Sonogashira coupling.

2. Experimental

2.1. Procedure for 3, 5-dimethyl-1-(2-nitrophenyl)-1H-pyrazole (C):

To a solution of acetyl acetone (2.002 g, 20 mmol), 2-nitrophenylhydrazine (3.369 g, 22 mmol), in ethanol (60 ml) was added five drops of con. HCl and heated at 50 ^{o}C for 1 h. After confirming the formation of 3, 5-dimethyl-1-(2-nitrophenyl)-1H-pyrazole by TLC, ice cooled water is added in to the reaction mixture. The precipitate was filtered, washed with water and then hexane. The product was formed as a yellow precipitate, filtered by normal filter paper. The product was recrystallized in ethanol.

Brown solid, 95% (4.1265 g), m.p 78 ^{o}C, IR (ν, cm^{-1}): 3444, 2923, 2104, 1612, 1527, 1359, 1118, 785. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 1H, J = 8 Hz), 7.72 (t, 1H, J = 8 Hz), 7.59 (t, 1H, J = 8 Hz), 7.50 (d, 1H, J = 8 Hz), 6.03 (s, 1H), 2.25 (s, 3H), 2.19 (s, 3H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 150.52, 146.43, 141.01, 133.23, 133.17, 129.54, 129.28, 125.12, 106.87, 13.50, 11.36. HRMS (ESI): m/z [M + H]$^{+}$ calcd for: $C_{11}H_{11}N_3O_2$ Calculated=217.2239, found= 217.2238.

2.2. Procedure for 2-(3, 5-dimethyl-1H-pyrazol-1-yl) aniline (D):

To a solution of 3, 5-dimethyl-1-(2-nitrophenyl)-1H-pyrazole (3.8 g, 17.49 mmol) in ethanol (50 ml) at 0 ^{o}C $SnCl_2$ (17.165 g, 76.07 mmol) was added portion wise over a period of 10 min. After complete addition of $SnCl_2$, the reaction mixture was slowly brought to room temperature and then refluxed for 4 h. After the completion of the reaction, ice-cold water was added to the reaction mixture and neutralized with 20% NaOH. The compound was extracted with ethyl acetate, dried over anhydrous sodium sulphate concentrated under reduced pressure to get light brown powder. The product was pure enough and used as such in the next reaction without column chromatographic purification.

Light brownish solid, 78%, (2.5548 g) m.p 79 ^{o}C, IR (ν, cm^{-1}): 3419, 2916, 1629, 1506, 1029, 746. ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.41 (m, 4H, J = 4, 4 Hz), 7.25 (s, 1H), 5.42 (s, 2H), 3.54 (s, 3H), 3.40 (s, 3H). ^{13}C NMR (75 MHz, CDCl3): δ 153.75, 148.64, 145.39, 134.13, 132.24, 129.94, 122.15, 121.26, 110.35, 18.42, 16.23. HRMS (ESI): m/z [M + H]$^{+}$ calcd for: $C_{11}H_{13}N_3$ Calculated=187.2410, found= 187.2411.

2.3. Procedure for Ligand synthesis (E):

A pressure tube was charged with 2-(3, 5-dimethyl-1H-pyrazol-1-yl) aniline (187.24 mg, 1 mmol), 2-hyroxy-1-naphthaldehyde (172.18 mg, 1 mmol), NH_4OAc (77. 08 mg, 1 mmol) and ethanol (3 ml) and was heated at 75 ^{o}C for 12 h. After confirming the formation of pyrazole derivative by TLC, ice cooled water was added in to the reaction mixture and was extracted with ethyl acetate, dried over anhydrous sodium sulphate concentrated under reduced pressure to get reddish brown semi solid as crude which was purified by column chromatography (silica gel) using pet.ether/ethyl acetate (80:20) to get pure compound. Reddish brown gummy compound, 94% (319 mg), m.p 72 ^{o}C, IR (ν, cm^{-1}): 3425, 2916, 1618, 1550, 1165, 746. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.55 (s, 1H), 9.15 (s, 1H), 8.02 (t, 1H, J = 8, 8 Hz), 7.81 (t, 1H, J = 12, 8 Hz), 7.73 (t, 1H, J = 8, 8 Hz), 7.57 (m, 3H, J = 8, 4 Hz), 7.42 (m, 2H, J = 8, 12 Hz), 7.19 (t, 1H, J = 8, 8 Hz) 7.07 (t, 1H, J = 12, 8 Hz), 2.32 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.40, 158.05, 143.33, 140.78, 136.30, 132.99, 132.51, 130.02, 129.20, 127.96, 127.32, 126.68, 123.56, 121.08, 120.43, 119.22, 117.63, 116.46, 109.20, 106.04, 13.57, 11.24. HRMS (ESI): m/z [M + H]$^{+}$ calcd for: $C_{22}H_{19}N_3O$ Calculated=341.4058, found= 341.4060.

2.4. Crystal data for Ligand:

$C_{22}H_{19}N_3O$, M = 341.40, Triclinic, a = 8.6171(4) Å, b = 10.4517(5) Å, c = 11.0784(5) Å, α= 106.316(4)°, β= 105.706(3)°, γ = 102.641(2)°, U = 873.60(7) Å^3, T = 293(2) K, Space group P-1, Z = 2, Reflections collected in 19699, Independent reflections in 3436 [R(int) = 0.0291], which were used in all calculation. The final wR_2 = 0.1374 (all data).

2.5. Procedure for Palladium complex (F):

In a 50 mL round bottom flask, $Pd(OAc)_2$ (074.42 mg, 0.3315 mmol) and 45.0 mg of NaCl (0.7715 mmol) were suspended in 6 mL of deionized water and stirred for 4 h until a clear solution was obtained. To this solution, (E)-1-(((2-(3,5-dimethyl-1H-pyrazol-1 yl)phenyl)imino)methyl)naphthalen-2-ol (230.44 mg, 0.675 mmol) in methanol (3 mL) was added drop wise and stirred for another 24 h. The reaction mixture was diluted with water, filtered, washed sequentially with water, methanol and *n*-hexane. The dark brown powder compound was air-dried and used for reaction.

93% yied. m.p 252 ^{o}C, IR (ν, cm^{-1}): 3419, 2140, 1641, 1436, 1317, 1020, 952. EDAX Analysis: Carbon (46.39 atomic %), Nitrogen, (21.25 atomic %), Oxygen (14.58 atomic %), Chlorin (5.38%), Palladium (12.40 atomic %).

2.6. General procedure for Suzuki-Miyaura coupling reactions (G):

In a 50 mL round bottom flask, we took aryl halide (1 eq) and Aryl boronic acid (1.2 eq) it was dissolved with EtOH/H_2O mixture in 1:1 ratio *i.e.* 5 mL of EtOH and 5 mL of H_2O. To this mixture, K_2CO_3 (2 eq) and Pd-Catalyst (0.05 mol %) are added. This reaction was allowed to stir at room temperature for 1-2 h, and then the desired coupled product will form. It was purified by column chromatography (silica gel) using pet.ether/ethyl acetate (80:20) to get pure compound.

N-([1,1'-biphenyl]-4-yl)acetamide- G(i): White colour powder, 82%, m.p 170 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, 1H, *J* = 6 Hz), 7.79 (d, 1H, *J* = 3 Hz), 7.61 (d, 1H, *J* = 6 Hz), 7.55 (t, 1H, *J* = 9 Hz), 7.43 (t, 6H, *J* = 6 Hz), 2.16 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.83, 137.32, 135.98, 132.32, 128.16, 128.12, 121.83, 117.29, 24.94.

3-nitro-1,1'-biphenyl – G(ii): Milky white solid, 86%, m.p 62 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.27 (d, 1H, *J* = 9 Hz), 8.09 (t, 1H, *J* = 6, 9 Hz), 7.76 (d, 1H, *J* = 6 Hz), 7.64 (m, 5H, *J* = 9, 6 Hz).

[1,1'-biphenyl]-4-amine – G(iii): Milky white solid, 80%, m.p 130 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, 2H, *J* = 9 Hz), 7.75 (d, 1H, *J* = 6 Hz), 7.64 (t, 2H, *J* = 9, 6 Hz), 7.54 (m, 4H, *J* = 6, 6 Hz), 4.64 (s, 2H).

4-(trifluoromethyl)-[1,1'-biphenyl]-2-amine – G(iv): White powder, 79%, m.p 120 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, 4H, *J* = 9 Hz), 7.40 (m, 6H, *J* = 6, 6 Hz).

3-(trifluoromethyl)-[1,1'-biphenyl]-2-amine – G(v):

Milky white solid, 87%, m.p 128 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (t, 4H, *J* = 6 Hz), 7.37 (m, 6H, *J* = 6, 6 Hz).

5,6-difluoro-[1,1'-biphenyl]-2-amine - G(vi): Yellow solid, 84%, m.p 172 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, 2H, *J* = 6 Hz), 8.18 (d, 2H, *J* = 6 Hz), 7.56 (m, 4H, *J* = 6, 6 Hz), 7.41 (t, 1H, *J* = 6 Hz), 7.64 (m, 5H, *J* = 6, 3 Hz).

2.7. General procedure for Sonogashira coupling reactions (H):

In 50 mL round bottom flask was charged with aryl halide (1 eq), and Phenyl acetylene (1.2 eq) it was dissolved with 5 ml of DMF. In this mixture Et_3N (1.2 eq), Pd-Catalyst (0.05 mol%) and CuI (0.1 mol %) are added. Then this reaction mixture has exposed to the temperature of 80 °C for around 6-12 h. After the completion of the reaction it was purified by column chromatography (silica gel) using pet.ether/ethyl acetate (80:20) to get the pure compound.

1,2-diphenylethyne – H(i): White crystals, 92%, m.p 65 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (dd, 4H, *J* = 6, 3 Hz), 7.41 (m, 6H, *J* = 3, 6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.46, 129.16, 128.40, 121.77, 81.52.

4-(phenylethynyl)aniline – H(ii): Yellow solid, 94%, m.p 128 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, 4H, *J* = 6, Hz), 7.64 (t, 2H, *J* = 6, 9 Hz), 7.55 (t, 3H, *J* = 6, 9 Hz), 4.68 (s, 2H).

N-(4-(phenylethynyl)phenyl)acetamide –H(iii): Light white solid, 85%, m.p 110 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, 4H, *J* = 6 Hz), 7.36 (d, 5H, *J* = 6 Hz), 1.26 (s, 3H).

1-nitro-3-(phenylethynyl)benzene – H(iv): Brownish solid, 88%, m.p 65 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (t, 4H, *J* = 6 Hz), 7.41 (m, 5H, *J* = 6, 6 Hz).

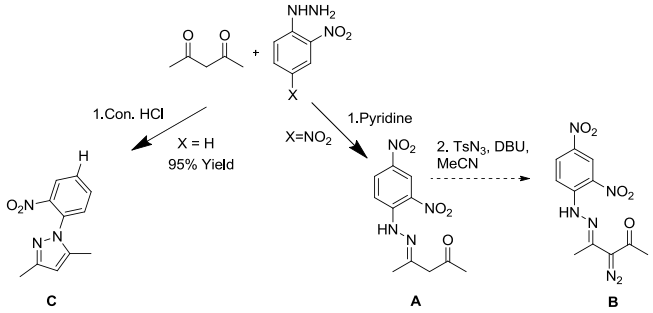
2.8. General procedure for Heck coupling reactions (I):

A pressure tube was charged with Aryl halide (1 m.mol), and Styrene (1.5 m.mol) dissolved with 5 mL of dry DMF. Then 0.01 mol% Palladium catalyst and K_2CO_3 (2 m.mol) are added, the reaction is stirred at 130 °C for 24 h. After the completion of the reaction, it was purified by column chromatography to get pure compounds.

(E)-(3-ethoxybuta-1,3-dien-1-yl)benzene: Brownish oily compound, 79%, ^{1}H NMR (300 MHz, DMSO): δ 7.97 (s, 5H), 7.28 (q, 1H, *J* = 6, 9 Hz), 6.93 (q, 1H, *J* = 9, 9 Hz), 4.78 (s, 2H), 3.8 (t, 2H, *J* = 9, 12 Hz), 2.17 (s, 3H). ^{13}C NMR (75 MHz, DMSO): δ 162.63, 138.12, 129.73, 129.41, 120.57, 116.49, 114.38, 113.84, 55.06, 31.26.

3. Results and Discussion

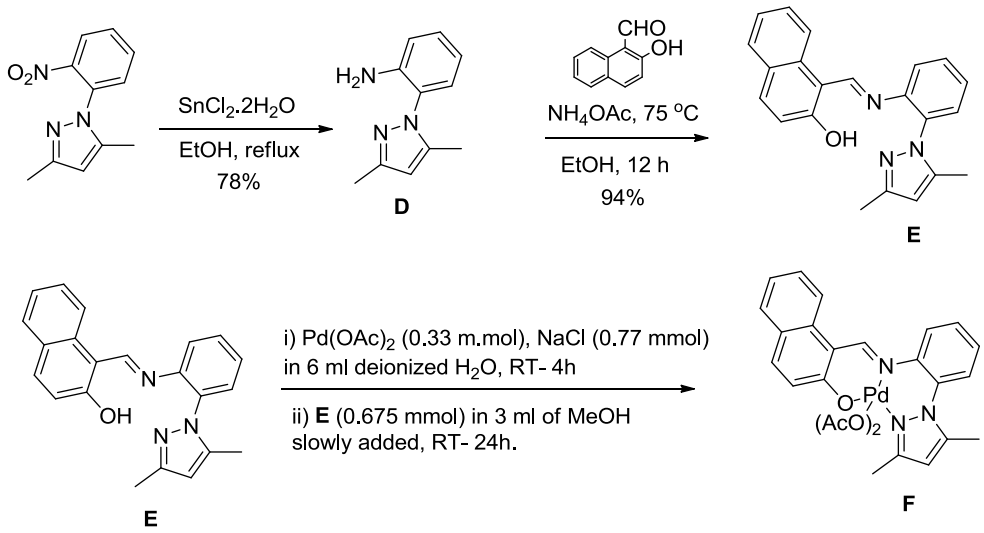
During the synthesis of α-diazo imines [31-32], in continuation of our research, we surprisingly observed an interesting difference in the reaction pathway between 2-nitrophenyl hydrazine and 2, 4-dinitrophenylhydrazine in their reaction with 2, 4-pentadione. 2-nitrophenylhydrazine yielding the pyrazole derivative **C** *via* cyclization of the initially formed hydrazone. On the other hand 2, 4-dinitrophenylhydrazine resulted in imine **A** without further cyclization [33], which could be further converted to α-diazo hydrazone **B** *via* diazotization with TsN_3. The nucleophilicity of nitrogen in 2, 4-dinitrophenylhydrazine is comparatively less due to two electron withdrawing NO_2 groups and did not undergo cyclization whereas in 2-nitrophenylhydrazine the nucleophilicity is high enough to undergo cyclization and gives pyrazole derivatives (**Scheme 1**).



Scheme 1. Effects of withdrawing group

Although we were disappointed with this cyclization, we envisaged that the pyrazole derivative **C** could serve as a precursor to a novel tridentate ligand. Accordingly, the NO_2 group of pyrazole derivative **C** was reduced by

treating with $SnCl_2$ to give the corresponding amine **D** in excellent yield which was subsequently converted to imine ligand **E** by treating with 2-hydroxy-1-naphthaldehyde (**Scheme 2**). The overall yield of this synthetic route is 70 % and requires chromatographic separation for only one step. All the products were characterized by IR, NMR and Mass Spectroscopic techniques; the trident ligand was characterized undoubtedly by the single crystal X-ray diffraction technique.



Scheme 2. Synthesis of Tridentate ligand and catalyst

From the single crystal structure of the ligand **E** (**Fig.2**) it is clear that the phenyl ring and the pyrazole rings are in a different plane and perpendicular to each other. This orientation of groups makes the ligand non superimposable with its mirror image and should be chiral (atropisomerism) and could be used as chiral ligand in asymmetric synthesis. Since the present investigation of catalytic study involves achiral substrates, or products, we used the ligand as such without resolution.

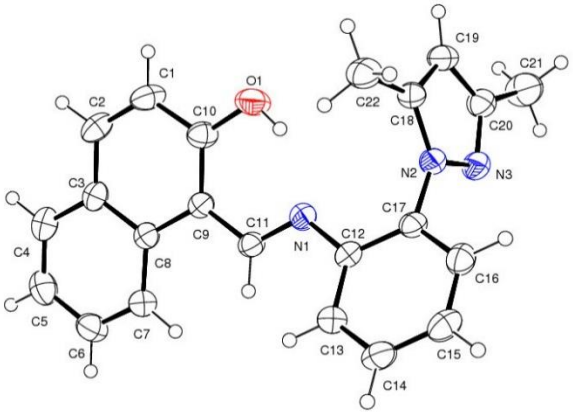
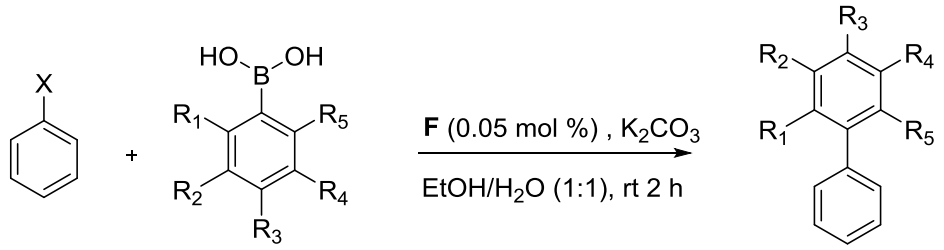


Fig. 2. ORTEP diagram of the Tridentate ligand E

The synthesis of palladium catalyst was achieved following the procedure reported by Petruci et al. [34] To a solution of $Pd(OAc)_2$ in deionized saline water the ligand **E** in ethanol was added and stirred for 24 h to get the catalyst **F**. The presence of metal in the catalyst was confirmed by EDAX analysis and it confirms the elemental composition values as follows, Carbon (46.39 atomic %), Nitrogen, (21.25 atomic %), Oxygen (14.58 atomic %), Chlorin (5.38%), Palladium (12.40 atomic %).

The catalyst was stable under room temperature and no loss of activity was observed over a period of two months. Our attempts to crystallize the catalyst in different solvent systems were not fruitful.

After the inclusion of the metal in the catalyst was confirmed, to study the efficiency of the catalyst, we carried out Suzuki coupling between iodobenzene and benzene boronic acid using 1 wt% of the catalyst in the presence of K_2CO_3 as the base in ethanol:water (1:1). Excellent yield was obtained in the room temperature itself within a short period of time (**Scheme 3**). Both bromo and iodo benzene resulted in the biphenyl with comparable yield and reactivity while chloro benzene failed to give biphenyl.

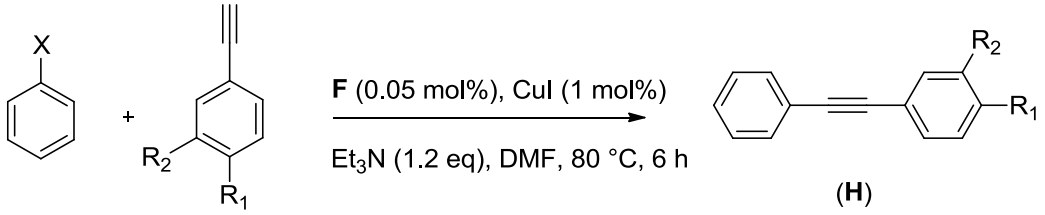


G (i)- X=I; R_1=H; R_2=H; R_3=$NHCOCH_3$; R_4=H; R_5= H; 82%
G (ii)- X=Br; R_1=H; R_2=NO_2; R_3=H; R_4=H; R_5= H; 86%
G (iiI)- X=I; R_1=H; R_2=H; R_3=NH_2; R_4=H; R_5= H; 80%
G (iv)- X=I; R_1=H; R_2=H; R_3=CF_3; R_4=H; R_5= NH_2; 79%
G (v)- X=Br; R_1=H; R_2=H; R_3=H; R_4=CF_3; R_5= NH_2; 87%
G (vi)- X=I; R_1=NH_2; R_2=H; R_3=H; R_4=F; R_5= F; 84%
G (vii)- X=Cl; R_1=H; R_2=H; R_3=CH; R_4=H; R_5= H; No reaction

(**G**)

Scheme 3. Suzuki-Miyaura coupling.

We were also interested to study the reactivity of Pd-catalyst to promote Sonogashira coupling reaction between iodobenzene and phenyl acetylene in DMF as solvent and Et_3N as base at 80 ºC. The yield was moderate and could not improve the yield appreciably by increasing the reaction time (12 h) or temperature (100 ºC). (**Scheme 4**)

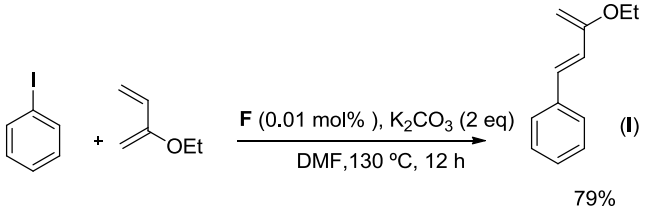


(**H**)

H (i)- X=I; R_1=H; R_2=H; 92%
H (ii)- X=I; R_1=NH_2; R_2=H; 94%
H (iii)- X=I; R_1=$NHCOCH_3$; R_2=H; 85%
H (iv)- X=Br; R_1=H; R_2=NO_2; 88%

Scheme 4. Sonogashira coupling

Finally, we screened the activity of Pd-catalyst for Heck coupling between iodo benzene and ethyl acrylate or styrene (**Scheme 5**). Good yields of ethyl cinnamate and trans stilbene were obtained even with 1 wt% of our catalyst. The products were confirmed by checking their melting point, and comparing TLC with their authentic compounds.



(**I**)

79%

Scheme 5. Heck coupling

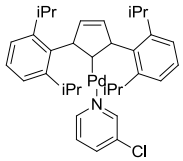
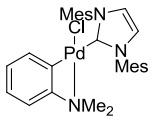
The results in **Table 1** clearly explained us, our catalyst **F** was the best catalyst in catalyst loading and reaction time category. In product yield, our results are almost close and better in some cases too.

4. Conclusions

We have achieved a simple and efficient route for the synthesis of a novel class of tridentate ligand and its phosphine free palladium complex to improve the reactivity and reduce the cost of catalyst for C-C cross coupling reactions with minimum catalytic loading. The catalytic activity of the Pd-catalyst has been studied for Suzuki coupling, Sonogashira and Heck coupling reactions. The complex is expected to be axially chiral and the enantiomers could be separated by resolution techniques. In the future we are going to attempt the separation of the two isomers via chiral salt formation

and crystallization or by changing suitable bulkier 1, 3-dione.

Table 1. Comparison of catalyst F with other reported catalysts

Entry	Reaction type	Catalyst	Catalyst loading (mol%)	Reaction time (h)	Product yield (%)	Reference
1	Suzuki	F	0.05	2	87	This work
2		$PdCl_2$(dppf)	20	12	78	35
3		Pd(IPr)cinnamyl	5	16	96	36
4			3	15	92	37
5		$Pd(acac)_2$	5	24	82	38
6		Pd-Au nanoparticle	5	4	95	39
7	Sonogashira	F	0.05	12	94	This work
8		$Pd(PPh_3)Cl_2$	3	25	98	40
9		$PdCl_2(PCy_3)_2$	3	12	94	41
10		$PdCl_2$(xantphos)	5	16	92	42
11		$Pd(OAc)_2$	5	24	64	43
12		Pd-zeolite	5	24	80	44
13	Heck	F	0.01	24	79	This work
14		$Pd(PPh_3)Cl_2$	5	36	96	45
15			2	18	92	46
16		$(Ar_2PtBu)_2PdCl_2$	2.5	24	90	47

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