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Poulami Pattanayak, Sankar Prasad Parua, Surajit Chattopadhyay

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Revised Mss Ms. Ref. No.: POLY-D-18-00676 Design and synthesis of immobilised orthopalladated catalyst for C-C coupling Poulami Pattanayak^a, Sankar Prasad Parua^a and Surajit Chattopadhyay^a*

^a Department of Chemistry, University of Kalyani, Kalyani 741235

Abstract

The new azo ligand 2-(2-(p-tolyldiazenyl)phenylamino)acetic acid, H_2L , [formulated as $H_3CC_6H_4$ -N = N-C₆H₄-N(H)(CH₂COOH)] was prepared. Reaction of H₂L with Na₂PdCl₄ afforded the orthopalladated mononuclear [(HL)PdCl] complexes. The uncoordinated free dangling carboxylic acid function was recognized and confirmed by x-ray crystallographic studies. The [(HL)PdCl] complex was immobilized on Merrifield resin tethering with the free carboxylic acid function of the complex. Catalytic activity of orthpalladated [(HL)PdCl] complex in homogeneous media and Merrifield supported immobilized complex in heterogeneous phase, toward Suzuki cross-coupling reactions, were examined.

Keywords

2-(2-(p-tolyldiazenyl)phenylamino)acetic acid; Pd(II); Orthometallation; Crystal structure; Heterogeneous catalyst; Suzuki reactions

*To whom corresponding should be addressed E-mail: scha8@rediffmail.com

1. Introduction

The importance and interest on the organometallic palladium complexes has grown during the last few decades owing to their involvement in unprecedented chemical transformations, either as reactive intermediate or as isolable stable precursor [1-8]. Further, the growing potential of this family of compounds as catalyst for the promotion of significant chemical reactions has been recognised as one of the fascinating area of chemical research [1-8].

Attempts to augment the catalytic efficiency of such orthopalladated complexes have been continuing in current chemical research. The molecular structure of the reported polymer anchored active catalysts had subtle uncertainty [9-13]. This work stems from our interest on synthesis of new catalytically active orthopalladated complexes of azo ligands. Studies on homogeneous Suzuki and Heck coupling reactions using different kinds of palladium complexes, incorporating azo ligands, as catalyst have been reported from our research group [14-18]. Further, we contemplated to prepare ligands and their catalytically active orthopalladated complexes, suitable for immobilisation on polymer support to fabricate the catalyst for exploiting those in heterogeneous phase. Polymers containing terminal halo substituted side chain have been utilised for the purpose of immobilising the catalytically active active complexes through any one of the free - $OH / -NH_2$ or - CO_2H functional groups present in the ligand backbone without changing the coordinating site [19-28].

The ligands were designed in such a manner so that a carboxyl group might hang about in the ligand framework, after formation of stable orthopalladated complex, for immobilisation on Merrifield resin as shown in Scheme 1.



Scheme 1

Herein we describe the synthesis, characterization and structure of H_2L , **1**, ligand and its orthopalladated complex. Immobilization of the new palladium complex on Merrifield resin and studies on the catalytic behaviour of the new palladium complex in homogeneous and heterogeneous phases toward C-C coupling reactions have been described in this paper.

2. Experimental

2.1. General consideration

All commercially available chemicals and solvents, utilized in the present work, were of analytical grade and in most cases these were used as obtained. 2-(p-tolyldiazenyl)aniline was prepared according to the reported procedure [29]. Ethyl bromoacetate, K₂CO₃, KOH were purchased from Sisco Research Laboratories (SRL), India. Chloromethylated polystyrene was purchased from Aldrich.

Microanalysis (C, H, N) was performed using a Perkin-Elmer 2400 C, H, N, S / O series II elemental analyzer. Infrared spectra were recorded on a Parkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV- 1800 PC spectrophotometer. ¹H NMR spectra were obtained on Brucker 400 NMR spectrometers in CDCl₃ using TMS as the internal standard. Surface morphology of functionalized polystyrene ligand and metal complex were analyzed using a scanning electron microscope (ZEISS EVO40, England) equipped with EDX facility.

2.2. Synthesis of Ligands

2.2.1. ethyl 2-(2-(p-tolyldiazenyl)phenylamino)acetate

To a solution of the 2-(p-tolyldiazenyl)aniline (2 g, 0.01 mol) in dry acetonitrile (30 mL), anhydrous K_2CO_3 (3.45 g, 0.025 mol) and ethyl bromoacetate (1.7g, 0.011 mol) were added. The mixture was refluxed for 8 h. The progress of the reaction was monitored by TLC. After filtering the mixture, the solvent of filtrate was removed under reduced pressure and the orange semi-solid residue was separated by column chromatography on silica gel (60 -120

mesh). The eluent was benzene-petroleum ether (8:2). R_f : 0.83. Upon evaporation of the solvent, the orange solid of pure ligand was obtained. Yield: 2.2g (82%). $C_{17}H_{19}N_3O_2$ (297): calcd.: C 68.67, H 6.44, N 14.13; found: C 68.62, H 6.40, N 14.06. Melting point: 78°C. IR (KBr) v = 3458 (NH), 1465 (N=N), 1740 (C=O). ¹H NMR (400MHz, CDCl₃): δ = 9.07 (s, 1H), 7.88-7.81 (m, 3H), 7.30 (d, 3H, J= 8), 6.84 (t, 1H, J=7.4), 6.64 (d, 1H, J=8), 4.31 (q, 2H), 4.08 (d, 2H, J=5.2), 2.42 (s, 3H), 1.33 (t, 3H, J= 7.2). ¹³C NMR (400MHz, CDCl₃): δ 170.31 (s,1C), 150.71 (s,1C), 142.14 (s,1C), 140.35 (s,1C), 136.75 (s, 1C), 132.29 (s,1C), 129.93 (s,1C), 129.75 (s,1C), 122.17 (s,1C), 116.58 (s,1C), 111.64 (s, 1C), 61.48 (s,1C), 45.09 (s, 1C), 21.46 (s,1C), 14.26 (s, 1C). UV-Vis (CH₂Cl₂): λ_{max} (ϵ , M⁻¹cm⁻¹)= 432 (15099), 322 (24211), 222 (31546).

2.2.2. 2-(2-(p-tolyldiazenyl)phenylamino)acetic acid; H₂L, 1

1 g (3.36×10^{-3} mol) of ethyl 2-(2-(p-tolyldiazenyl)phenylamino)acetate in 25 mL of ethanol was placed in a 100 ml round-bottomed flask mounted on a magnetic stirrer and the temperature was maintained at 35°C. 5 mL 1.4(M) KOH solution was added and stirring was continued. The reaction was quenched after 1h by addition of 50 ml of water. Unreacted ethyl 2-(2-(p-tolyldiazenyl)phenylamino)acetate was removed by ether extraction (2×25mL) and the aqueous part was acidified with 2(N) hydrochloric acid to bring the pH near 6. The H₂L ligand precipitated on standing and collected by filtration, dried under vacuum and recrystallised from ethanol. Yield: 0.75g (83%) C₁₅H₁₅N₃O₂ (269): calcd: C 66.90, H 5.16, N 15.60; found: C 66.85, H 5.65, N 15.65. Melting point: 103°C. IR (KBr) v = 1470 (N=N), 1721(C=O). ¹H NMR (400MHz, DMSO d6): δ = 8.67 (s, 1H), 7.83 (d, 2H, J= 8.4), 7.71 (d, 1H, J= 7.2), 7.38 (d, 2H, J=8), 7.32-7.28 (m, 1H), 6.77- 6.7 (m, 2H), 4.03 (s, 2H), 2.34 (s, 3H). ¹³C NMR (400MHz, DMSO d6): 150.65 (s,1C), 142.99 (s,1C), 140.26 (s, 1C), 135.88 (s,1C), 133.18 (s,1C), 130.25 (s,1C), 129.24 (s,1C), 122.17 (s,1C), 115.11 (s,1C), 114.33(s, 1C), 113.09 (s,1C), 70.17 (s, 1C), 21.39 (s, 1C). UV-Vis spectrum (CH₂Cl₂) λ_{max} (ϵ , M⁻¹cm⁻¹): 424 (9677), 323 (17460), 242 (15154).

2.3.Syntheses of Complexes

2.3.1. Synthesis of [(HL)PdCl] complex, 2

The H₂L (100 mg, 0.37 mmol) ligand was taken in round bottom flask in 10 mL methanol and acidified with 0.3 mL 2(N) aqueous solution of HCl with stirring. The 5 mL methanolic solution of Na₂PdCl₄ (108 mg, 0.37 mmol) was added drop wise into the acidified solution of H₂L. The color of the solution changed from light orange to brown. The mixture was stirred for 4h and kept standing for 24 hours. The crystalline product of [(HL)PdCl] was collected and further recrystallised from acetonitrile-dichlomethane mixture to obtain the crystals of pure product. Yield: 85 mg (56%). C₁₅H₁₃ClN₃O₂Pd, 0.5 CH₂Cl₂ (451): calcd. for C 41.27, H 3.10, N 9.32; found: C 41.20, H 3.05, N 9.25. Melting point: 233⁰C. IR (KBr) v = 3405 (NH), 1432 (N=N), 1720(C=O). ¹H NMR (400MHz, DMSO d6): δ = 7.88 (d, 1H, J= 8), 7.75 (d, 1H, J= 8), 7.64-7.57 (m, 2H), 7.39 (t, 1H, J= 7.6), 7.23 (t, 1H, J= 18), 7.04 (d, 1H, J=8), 6.62 (s, 1H), 4.31 (d, 2H), 2.19 (s, 3H). ¹³C NMR (400 MHz, DMSO d6): δ 165.39 (s,1C), 159.63 (s,1C), 151.70 (s,1C), 147.17 (s,1C), 143.53 (s, 1C), 136.17 (s,1C), 134.58 (s,1C), 130.03 (s,1C), 128.79 (s,1C), 128.30 (s,1C), 128.05 (s, 1C), 127.05 (s,1C), 117.81(s, 1C), 82.28 (s,1C), 22.48 (s, 1C). UV-Vis spectrum (CH₂Cl₂) λ_{max} (ϵ , M⁻¹cm⁻¹): 506(4267), 406(7209), 365(9982), 249(12364), 230(14681).

2.4. Immobilization of [(HL)PdCl] on Merrifield resin, 3

The [(HL)PdCl] complex (0.25 g) was dissolved in DMF (10 mL) and refluxed with Merrifield resin beads (0.5 g) for 10 h in presence of K₂CO₃. After that the resin was filtered and washed with large quantities of H₂O, methanol, ethanol, dichloromethane until the filtrate was colorless. The very dark brown beads were obtained after dried.

2.5. General experimental procedure for Suzuki cross-coupling reaction using [(HL)PdCl] in homogeneous media

A mixture of aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (2.0 mmol), THF (6.0 ml) and 0.5 mol% of Pd catalyst, [(HL)PdCl] was refluxed. To study the progress of the reaction the reaction mixtures were collected at different time interval and examined by TLC. At the end of the reaction, the solvent was evaporated and the residue was purified by chromatography on silica gel. The product was analyzed by ¹HNMR.

2.6. General experimental procedure for Suzuki cross-coupling reaction using $P \sim [(L)PdCl]$ in heterogeneous phase

A mixture of aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), THF (6.0 ml) and 2.26 mg of **P**~[(L)PdCl] catalyst was refluxed. To study the progress of the reaction, the reaction mixtures were collected at different time interval and examined by TLC. At the end of the reaction, the catalyst was separated by simple filtration. After evaporation of the solvent the residue was purified by chromatography on silica gel. The product was analyzed by ¹HNMR spectroscopy.

2.7. X-ray structure determination of [(HL)PdCl]

Single Crystal of [(HL)PdCl] was grown by slow evaporation of acetonitriledichlomethane mixture at 298 K. Data were collected on a Bruker SMART CCD diffractometer using Mo-K α monochromator (λ =0.71073). Structure solutions were performed using SHELXTL V 6.14 program package. [30]. Full matrix least square refinements on F2 were performed using SHELXTL V 6.14 program package. [30]. All the non-hydrogen atoms were refined anisotropically using full-matrix least squares method. Hydrogen atoms were included for structure factor calculations after placing them at calculated positions. Atomic coordinates and isotropic thermal parameters are of [(HL)PdCl] are given in **Table 1**

Chemical formula	$(C_{15}H_{12}ClN_3O_2Pd), 0.5CH_2Cl_2$	
Formula weight	451	
Crystal system	monoclinic	
space group	P21/c(No. 14)	*
<i>a</i> /Å	11.0247(17)	
<i>b</i> /Å	17.669(3)	
c/Å	18.167(3)	
α/deg	90	
β/deg	98.699(4)	
γ/deg	90	
λ /Å	0.71073	
$V/\text{\AA}^3$	3498.1(10)	
<i>F</i> (000)	1784	
Ζ	4	
T/K	296	
D/mg/m ⁻³	1.711	
μ /mm ⁻¹	1.378	
<i>R1</i> (all data)	0.0363	
$wR2[I > 2\sigma(I)]$	0.0910	
GOF	1.05	

Table 1. Crystal data collection and structure refinement parameter for [(HL)PdCl]

3. Results and Discussion

3.1. Synthesis of H₂L and [(HL)PdCl]

The newly designed ligand system, H_2L , **1**, was synthesized in two steps, starting from 2-(arylazo)aniline. In the first step ethyl-2-bromoacetate was treated with 2-(Arylazo)aniline in presence of anhydrous K_2CO_3 to obtain the new compound ethyl 2-(2-(aryldiazenyl) phenylamino) ethanoate, in excellent yield (Scheme 2). The desired ligand, H_2L , **1**, was obtained, in the second step, by alkaline hydrolysis of ethyl 2-(2-(aryldiazenyl) phenylamino)

ethanoate followed by acidification (Scheme 2). The H_2L ligand was characterized by spectroscopic studies (see below).



Scheme 2

The orthopalladated complex, [(HL)PdCl], **2**, was prepared by the reaction of Na₂PdCl₄ with acidified methanolic solution of H₂L ligand (Scheme 2). Crystalline crude product was isolated upon standing the reactions mixture for 36 hours at 28^oC. The crystals of pure complex were isolated by recrystallisation. Acetonitrile-dichlomethane mixed solvent was used for recrystallisation.

3.2. Characterization

The 2-(2-(*p*-tolyldiazenyl)phenylamino)ethanoic acid, H₂L, **1**, ligand display characteristic UV-Vis spectra. The transition in the visible region near 425 nm for H₂L was assigned for n $\rightarrow \pi^*$ transition [29,31,32]. The electronic spectrum of [(HL)PdCl], **2** was distinctly different from the corresponding ligand (**Figure 1**). The lowest energy absorption bands for [(HL)PdCl] was observed near 505 nm. Relevant data are collected in experimental section.



Figure 1. UV-Vis spectra of H₂L (—, 1.75×10^{-5} m) and [(HL)PdCl] (—, 1.2×10^{-5} m) in dichloromethane.

The IR spectra of all new compounds were recorded using KBr pellet. The 2-(2-(p-tolyldiazenyl) phenylamino) ethanoic acid, H₂L ligand displayed a single band near 1470 cm⁻¹ for $v_{N=N}$ which shifted to 1432 cm⁻¹ in [(HL)PdCl] indicating metal coordination to the azo nitrogen. The characteristic $v_{C=0}$ and v_{C-OH} of carboxylic group for H₂L appeared at 1720 cm⁻¹ and 1250 cm⁻¹ respectively, did not disappear or shift in considerable extent for [(HL)-PdCl] (1720 cm⁻¹ and 1240 cm⁻¹) signifying no interaction with the metal centre. Although the v_{NH} of H₂L did not appear distinctly due to broad overlapping band of v_{OH} of carboxyl group but the v_{NH} of the complex[(HL)PdCl] appeared distinctly at 3405 cm⁻¹ [32].

The H₂L, **1**, ligand, atom numbering scheme is shown in Figure **2**, displayed a well resolved ¹H-NMR spectrum. The N-H protons appeared at δ 8.67 for one equivalent proton [32]. The aromatic proton resonances were observed within δ 6.72 to δ 7.83. The methylene proton of C(14) appeared as doublet (due to coupling with N-H proton) at δ 4.03. The two doublets, at δ 7.38 and δ 7.83, each of two equivalent protons for C(3);C(5) and C(2);C(6) of H₂L were recognized in the ¹H-NMR spectra. The two doublets for C(9) and C(12) protons

appeared at δ 7.71 and δ 6.73 whereas two triplets for C(10) and C(11) protons were observed at δ 7.28 and δ 6.75.



Figure 2: Structural formula of H₂L

The [(HL)PdCl] complex i.e. the palladium complex of H₂L exhibited well resolved ¹H-NMR spectrum. The methylene proton of C(14) appeared as doublet at δ 4.25 and the –NHproton appeared as a broad band at δ 6.42 indicating coordination of amino nitrogen without dissociation of amino proton of the ligand [29]. The [(HL)PdCl] complex displayed a singlet at δ 7.23 assigned for C(3). In addition to that the of the ¹H-NMR spectrum exhibited three doublets (δ 7.88, 7.75 and 7.04) for one equivalent proton each, a triplet (at δ 7.39) for one equivalent proton and a quintet at (7.61) for two equivalent protons. The quintet has been attributed to a doublet and a triplet. Thus the pattern and the proton count is consistent with that of C(4), C(5), C(9), C(10), C(11), C(12) protons. The methyl proton of C(13) was observed at δ 2.19. The molecular structure of [(HL)PdCl] was confirmed by x-ray studies (see below). The ¹³C NMR spectra of the ligand H₂L and complex [(HL)PdCl] displayed thirteen and fifteen aromatic carbon resonances in the range δ 150.65 -21.39 and δ 165.39 – 22.48 respectively, consistent with the structural compositions of ligand H_2L and complex [(HL)PdCl]. 1H and ¹³C NMR data are given in Section 2. However, the prton resonance for carboxyl group could not be obtained after repetitive experiments, may be due to contaminated water in the DMSO-d₆ solvent [33]. The broad signal of very high intensity near δ 3.5 indicated the water contamination.

3.3. X-ray structure

The x-ray structure of [(HL)PdCl] complex, **2** was determined for unequivocal characterization. The asymmetric unit consists of two [(HL)PdCl] complexes and one solvent (dichloromethane) molecule. The bond parameters of two palladium complexes of asymmetric unit are very close to infer that those are same. The perspective view of the molecule has been shown in **Figure 3**. Selected bond distances and angles are collected in **Table 2**.



Figure 3. Crystal structure of [(HL)PdCl] (2). Hydrogen atoms and solvent molecule are

omitted for clarity

 Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound [(HL)PdCl]

Bond Distances					
Pd1-Cl1	2.329(3)	N3-C7	1.398(12)		
Pd1-N1	2.191(7)	C1-C2	1.393(15)		
Pd1-N2	1.937(7)	C7-C8	1.379(15)		
Pd1-C12	1.960(9)	C7-C12	1.415(14)		
N1-C1	1.456(12)	C13-C14	1.508(14)		
N1-C13	1.476(12)	O1-C14	1.183(14)		
N2-N3	1.275(10)	O2-C14	1.315(13)		
N2-C2	1.410(11)				
Bond Angles					
Cl1-Pd1-N1	99.3(2)	N2-C2-C3	122.4(9)		

Cl1-Pd1-N2	177.6(2)	N2-C2-C1	115.7(8)
Cl1-Pd1-C12	100.0(3)	N3-C7-C12	117.0(9)
N1-Pd1-N2	81.3(3)	N3-C7-C8	121.1(9)
N1-Pd1-C12	160.2(3)	Pd1-C12-C7	111.4(6)
N2-Pd1-C12	79.3(3)	Pd1-C12-C11	132.9(7)
N1-C1-C6	123.7(9)		

The molecular structure confirmed orthopalladation and tridentate (C,N,N) binding mode of monoanionic ligand (HL)⁻. In addition, a chloride ligand satisfied the tetra coordination about palladium (II) centre and the geometry of the coordination sphere was distorted square planar. Further, the x-ray structure confirmed the presence of uncoordinated free dangling carboxyl group. The Pd-C and Pd-Cl distances are within the normal range whereas Pd-N1 distance (2.191 Å) is longer than the Pd-N2 distance (1.937 Å) as a result of stronger trans effect of aryl carbon atom (C(12)) [29]. The molecules of [(HL)PdCl] complex form infinite array of hydrogen bonded tetrameric units via hydrogen bonded carboxylic acid function. In each unit of the array, the tetramers are held together through N...Cl...O hydrogen bonds [34,35]. A part of the infinite array is shown in **Figure 4** where the tetrameric unit has been shown in the box.





3.4. Homogeneous catalysis

The catalytic activity of [(HL)PdCl] toward C-C coupling reactions in homogeneous media was necessary to be examined before immobilization on polymer support. Therefore, this

complex was used as catalyst for Suzuki coupling reactions in homogeneous media *i.e.* in THF (Scheme 3) under usual atmospheric condition.



The complex exhibited fairly good efficacy as catalyst for Suzuki coupling reactions. The isolated yields, reaction time and amount of catalyst used are given in **Table 3**.

3.5. Immobilization of [(HL)PdCl] in Merrifield resin and characterization

The chemical composition of Merrifield resin bead is chloromethylated polystyrene, formulated as $-[-CH_2-CH(C_6H_4-CH_2CI)-]_n$. Although, tethering of carboxyl group with the Merrifield Resin is well known but scarcely utilized for the immobilization of ligands or complexes to prepare heterogeneous catalysts [13, 37-41]. Binding of carboxylic acid function of the amino acid on the resin bead during solid phase peptide synthesis encouraged us to utilize the free carboxylic acid function of [(HL)PdCl] for anchoring with the Merrifield resin by forming C-O bond formation. Thus, the [(HL)PdCl], **2**, complex was refluxed with Merrifield resin beads in DMF solvent in presence of K₂CO₃ to obtain the immobilised catalyst **P**~[(L)PdCl], **3** (Scheme 4). Absence of sharp band at 1240 cm⁻¹ of free [(HL)PdCl] for vcoo⁻ and 1264 cm⁻¹ for vc-cl of Merrifield resin



(a)Na₂PdCl₄, CH₃CN, Reflux, 3h (b) Merrifield resin, K₂CO₃ DMF, Reflux, 4h Scheme 4

in the **P**~[(L)PdCl], **3** indicated the formation **P**~[(L)PdCl]. The SEM images and EDX spectrum of **P**~[(L)PdCl] have been shown in **Figure 4** and **Figure 5**. The morphological changes are visible in the SEM image and the EDX shows the presence of palladium which are consistent with the formation of **P**~[(L)PdCl], **3**.



Figure 4. SEM images of Merrifield resin (A) and P~[(L)PdCl] complex (B)



Figure 5. EDX spectra of P~[(L)PdCl] complex

3.6. Heterogeneous catalysis

Keeping in view the application and interest on palladium based heterogeneous catalysts in academia and industry, there is a need to design and develop active, re-usable and easily recoverable chemically supported heterogeneous palladium catalysts [13,38,42-46]. The P~[(L)PdCl] has been used as catalyst for Suzuki cross coupling reactions and it was found that this heterogeneous catalyst was efficient for such catalysis (results are collected in **Table 3**).

Although the inclusion of [(HL)PdCl] in Merrifield resin could be detected by EDX but the loading of catalyst could not be determined quantitatively. For each reaction in heterogeneous phase weighted amount of **P**~ [(L)PdCl] beads were added as catalyst.

Table 3. Assessment of catalytic activity in Suzuki cross coupling reaction catalysed by P~

			// ``	% yield	
Entry	Aryl halide	Product	lime (h)	[(HL)PdCl]	P~ [(L)PdCl]
1.	⟨		4	60	80
2			3	75	90
_{З.} Ме	0-	MeO-	4	65	75
4.Et	о-{	EtO-	4	68	76
5.			3	70	80
6.			4	76	85

[(L)PdCl], 3 and [(HL)PdCl], 2

Further, the \mathbf{P} ~ [(L)PdCl] species could be reused as catalyst (up to three times were checked) without much difference in isolated yields. However, the higher yield than the homogenous process is attributed to ease of isolation of products.

4. Conclusions

New azo ligand with free carboxylic acid function has been synthesized and form that the new orthometallated palladium complex has been prepared. The newly synthesized orthopalladated complex contains uncoordinated pendant carboxylic acid function. The new

complex was efficient catalyst for Suzuki C-C coupling reactions in homogeneous media. The free pendant carboxylic acid function of palladium complex has been utilized to immobilize the palladium complex on Merrifield resin. The immobilized catalyst exhibited catalytic efficacy toward Suzuki C-C coupling reactions keeping it in heterogeneous media.

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Appendix A. Supplementary materials

CCDC 1012256 for **2** contains the supplementary crystallographic data. Figures S1-S13 represents the UV-Vis; IR, ¹H NMR and ¹³C NMR spectra of ligand and complexes. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>. Supplementary data associated with this article can be found, in the online version, at http://..

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Design and synthesis of immobilised orthopalladated catalyst for C-C coupling



Graphical Abstract Synopsis

Design and synthesis of immobilised orthopalladated catalyst for C-C coupling

Poulami Pattanayak^a, Sankar Prasad Parua^a and Surajit Chattopadhyay^{a*}

^a Department of Chemistry, University of Kalyani, Kalyani 741235



New orthopalladated complex was synthesized and characterized unequivocally prior to immobilization on polymer support through the free carboxylic acid function. The newly synthesized palladium complex was active as catalyst for C-C coupling reactions in homogeneous media. Thus it was anchored on Merrifield resin. This polymer supported catalyst exhibited good efficacy as catalyst toward C-C coupling reactions.

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