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# Tetranuclear assembly of palladium(II): Catalyst for C–C coupling reactions

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### ABSTRACT

The 2-((2-benzylamino)phenyldiazenyl)phenol,  $H_2OL$  [where  $H_2OL = ArOHN = NC_6H_4N(H)CH_2(C_6H_5)$ ; Ar =  $C_6H_5$  (for  $H_2OL^1$ ), *p*-MeC<sub>6</sub>H<sub>4</sub> (for  $H_2OL^2$ ) or *p*-ClC<sub>6</sub>H<sub>4</sub> (for  $H_2OL^3$ )], ligands were prepared by the reaction of the appropriate 2-((2-hydroxyaryl)azo)anilines with benzyl bromide. The reactions of Na<sub>2</sub>PdCl<sub>4</sub> with  $H_2OL$  afforded tetranuclear Pd(II) complexes of the composition [Pd(OL)]<sub>4</sub>. The ligands bind palladium(II) in a tridentate (N, N, O) fashion. The X-ray structure of [Pd(OL<sup>1</sup>)]<sub>4</sub> was determined to confirm the characterization. The newly synthesized [Pd(OL<sup>1</sup>)]<sub>4</sub> complex was utilized as a catalyst for the Suzuki and Heck reaction for a variety of substrates.

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#### 1. Introduction

The appropriate ligands have been designed and used for the synthesis of structurally diverse tetranuclear palladium(II) complexes. Different types of bridging to hold the four square planar palladium(II) units were found to be the basis of structural diversity within the tetranuclear assemblies [1–10]. A structure containing bridging phenoxo oxygens and two nitrogen coordinations is only known in one case [11]. Earlier, we have shown that azo ligands of type **1** afforded only mononuclear complexes of Pd(II) coordinating through (C, N, N) or (N, N, N) modes [12–15].



attracted attention in current chemical research [19–53]. As a result we have designed and synthesized the appropriate mononu-

clear palladium(II) complexes incorporating azo ligands which

exhibited satisfactory results toward catalytic C-C coupling reac-

tions [19-53]. Both challenges, i.e., to prepare tetranuclear palla-

dium(II) complexes and to examine their effectiveness as

catalysts toward C-C coupling reactions, encouraged us to carry

out the present work. Therefore, we contemplated to design and

synthesize (N, N, O) coordinating ligands, 2, where the phenoxo

oxygen may be available as a bridging atom, and to study the Heck

and Suzuki coupling reactions using one of the newly synthesized

Recently, it was shown that (C, N, O) coordinating Schiff base ligands afforded tetranuclear palladium complexes [16–18]. The use of palladium(II) mononuclear complexes as efficient catalysts in homogenous and heterogeneous C–C coupling reactions has

In this paper, the syntheses of the newly designed ligands and corresponding tetranuclear palladium(II) complexes, including characterization, have been described. The catalytic behavior of one of the newly synthesized complexes toward C–C coupling reactions has also been described.





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#### 2. Experimental

#### 2.1. Materials

The solvents used in the reactions were of reagent grade (E. Merck, Kolkata, India) and were purified and dried by the reported procedures [54]. Palladium chloride was obtained from Arora Matthey, Kolkata, India. Na<sub>2</sub>[PdCl<sub>4</sub>] was prepared following a reported procedure [55]. The 2-((2-hydroxyaryl)azo)anilines were prepared according to the reported procedures [56,57]. Benzyl bromide and potassium carbonate were purchased from E. Merck, Kolkata, India. Phenylboronic acid, iodobenzene, bromobenzene, 1-iodo-3,5-dimethylbenzene, 1-iodo-3,4-dimethylbenzene, 1-iodo-2-nitrobenzene, 1-bromo-2-nitrobenzene and styrene were purchased from Aldrich.

#### 2.2. Physical measurements

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 Perkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer. <sup>1</sup>H NMR spectra were obtained on Brucker 400 spectrometers in CDCl<sub>3</sub>.

#### 2.3. Syntheses of the ligands

All the ligands,  $H_2OL^1$ ,  $H_2OL^2$  and  $H_2OL^3$ , were prepared following similar procedures. A representative procedure for  $H_2OL^1$  is given below.

#### 2.3.1. Syntheses of $H_2OL^1$

mixture of 2-((2-hydroxyphenyl)azo)aniline (0.3 g. Α 1.52 mmol), benzyl bromide (0.27 g, 1.52 mmol), pyridine and a catalytic amount of KI in 30 cm<sup>3</sup> dry acetonitrile was refluxed for 10 h. The orange liquid mass that was obtained after evaporation of the solvent afforded the crude ligand, H<sub>2</sub>OL<sup>1</sup>, which was isolated by column chromatography on silica gel (60-120 mesh) using the eluent petroleum ether: benzene (9:1 v/v). Upon evaporation of the solvent after chromatography, the orange-red solid of pure H<sub>2</sub>OL<sup>1</sup> was obtained. Yield: 50%. Anal. Calc. for C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>O: C, 75.2; H, 5.6; N, 13.8. Found: C, 75.2; H, 5.5; N, 13.8%. UV-Vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max},~nm~(\epsilon,~M^{-1}~cm^{-1}):~478~(3700),~318~(3616),~251~(3926),~230~(4120).~IR~(KBr,~cm^{-1}):~3381~(OH),~3031~(NH),~1454~(N=N).~^1H$ NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 12.95 (s, OH), 9.56 (s, NH) 8.04 (s, 1H), 7.95 (d, 1H), 7.68 (d, 1H), 7.52-7.49 (m, 1H), 7.45-7.41 (m, 1H), 7.40-7.37 (m, 1H), 7.35-7.32 (m, 1H), 7.28-7.22 (m, 2H), 6.99-6.94 (m, 2H), 6.84-6.78 (m, 2H), 4.55 (d, 2H).

#### 2.3.2. Syntheses of $H_2OL^2$ and $H_2OL^3$

The ligands  $H_2OL^2$  and  $H_2OL^3$  were prepared using 2-((2-hydroxytolyl)azo)aniline and 2-((2-hydroxy-4-chloro)azo)aniline in place of 2-((2-hydroxyphenyl)azo)aniline, respectively.

Yield: 55%. *Anal.* Calc. for  $C_{20}H_{19}N_3O$ : C, 75.7; H, 5.9; N, 13.2. Found: C, 75.7; H, 6.1; N, 13.3%. UV–Vis spectrum  $(CH_2Cl_2) \lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 476 (4240), 326 (3913), 256 (4000), 226 (4720). IR (KBr, cm<sup>-1</sup>): 3370 (OH), 3031 (NH), 1453 (N=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 12.99 (s, OH), 9.47 (s, NH), 7.65 (d, 1H), 7.39–7.37 (m, 5H), 7.33–7.31 (m, 1H), 7.25 (t, 2H), 6.82–6.77 (m, 3H), 4.54 (d, 2H), 2.35 (s, 3H).

Yield: 50%. Anal. Calc. for  $C_{19}H_{16}N_3Cl$ : C, 67.5; H, 4.7; N, 12.4. Found: C, 67.6; H, 4.7; N, 12.5%. UV–Vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 482 (3500), 325 (3296), 250 (3460), 227 (3966). IR (KBr, cm<sup>-1</sup>): 3380 (OH), 3039 (NH), 1506 (N=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 13.20 (s, OH), 9.50 (s, NH) 8.91 (d, 1H), 7.68–7.54 (m, 3H), 7.43–7.35 (m, 2H), 7.27–7.21 (m, 1H), 7.10 (d, 1H), 6.98 (d, 1H), 6.93–6.89 (m, 2H), 4.54 (d, 2H).

#### 2.4. Syntheses of the complexes

The complexes,  $[Pd(OL^1)]_4$ ,  $[Pd(OL^2)]_4$  and  $[Pd(OL^3)]_4$  were prepared following similar procedures. A representative procedure for  $[Pd(OL^1)]_4$  is given below.

#### 2.4.1. Syntheses of $[Pd(OL^1)]_4$

A solution of  $H_2OL^1$  (0.146 g, 0.52 mmol) in 15 cm<sup>3</sup> methanol was added to a solution of Na<sub>2</sub>PdCl<sub>4</sub> (0.153 g, 0.52 mmol) in 10 cm<sup>3</sup> methanol. The mixture was stirred for 12 h under slightly warm conditions. The dark solid precipitate was separated by filtration and purified by column chromatography using silica gel (60–120 mesh). The eluent was benzene:acetonitrile (95:5 v/v) mixed solvent. Upon evaporation of the solvent, a blue–violet solid of pure [Pd(OL<sup>1</sup>)]<sub>4</sub> was obtained. Yield: 50%. *Anal.* Calc. for C<sub>76</sub>H<sub>60-</sub>N<sub>12</sub>O<sub>4</sub>Pd<sub>4</sub>: C, 55.9; H, 3.6; N, 10.3. Found: C, 56.0; H, 3.6; N, 10.3%. UV–Vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 556 (27245), 421 (24311), 343 (17283), 273 (49264), 228 (100000). IR (KBr, cm<sup>-1</sup>): 1337 (N=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 7.59 (d, 1H), 7.53 (d, 1H), 7.39 (d, 1H), 7.09–6.99 (m, 3H), 6.74 (t, 1H), 6.66–6.60 (m, 2H), 6.37 (d, 1H), 4.83 (d, 1H), 3.15 (d, 1H).

2.4.2. Syntheses of  $[Pd(OL^2)]_4$  and  $[Pd(OL^3)]_4$ 

The complexes  $[Pd(OL^2)]_4$  and  $[Pd(OL^3)]_4$  were prepared using  $H_2OL^2$  and  $H_2OL^3$  in place of  $H_2OL^1$ , respectively.

[ $Pd(OL^2)$ ]<sub>4</sub>. Yield 60%. Anal. Calc. for C<sub>77</sub>H<sub>62</sub>N<sub>12</sub>O<sub>4</sub>Pd<sub>4</sub>: C, 56.2; H, 3.7; N, 10.2. Found: C, 56.2; H, 3.7; N, 10.1%. UV–Vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 557 (25030), 417 (18696), 345 (15222), 272 (41140), 226 (71185). IR (KBr, cm<sup>-1</sup>): 1333 (N=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 7.33–7.29 (m, 3H), 7.01–6.96 (m, 2H), 6.93 (t, 1H), 6.60 (d, 2H), 6.53 (t, 1H), 6.38 (t, 1H); 6.31 (d, 1H), 4.72 (d, 1H), 3.75 (d, 1H), 2.34 (s, 3H).

[*Pd*(*OL*<sup>3</sup>)]<sub>4</sub>. Yield 60%. *Anal.* Calc. for C<sub>76</sub>H<sub>59</sub>N<sub>12</sub>O<sub>4</sub>Pd<sub>4</sub>Cl: C, 54.8; H, 3.5; N, 10.1. Found: C, 54.9; H, 3.5; N, 10.0%. UV–Vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 556 (29805), 417 (24436), 343 (18640), 273 (51766), 228 (103398). IR (KBr, cm<sup>-1</sup>): 1334 (N=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 7.58 (d, 1H), 7.52 (d, 1H), 7.44–7.38 (m, 2H), 7.35 (s, 1H), 7.13–7.06 (m, 3H), 6.73 (d, 1H), 6.68–6.62 (m, 1H), 6.45 (d, 1H), 4.80 (d, 1H), 3.34 (d, 1H).

2.5. General procedures for the Suzuki cross coupling reaction and isolation of the catalyst

In an oven dried round bottomed flask a mixture of phenyl boronic acid (0.244 g, 2.0 mmol), aryl halide (2.0 mmol), the palladium complex [Pd(OL<sup>1</sup>)]<sub>4</sub> (0.002 mmol) and potassium carbonate (0.145 g, 2.5 mmol) in THF  $(10 \text{ cm}^3)$  was heated to reflux for 2 h, as mentioned in Table 2. After the reaction was completed, the solvent was evaporated and the reaction mixture was extracted with diethyl ether. The ether solution was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The ether solution, containing the reaction mixture, was passed through a 30.48 cm silica column (60-120 mesh), the complex was not separated out and it remained trapped in the column. After the desired compound was extracted from the column, the complex was extracted using dichloromethane. The unchanged complex was used twice. After evaporation of the ether, solids of the pure products were obtained. The yields of the products obtained from all the reactions were determined after isolation, and the products were characterized by <sup>1</sup>H NMR spectra.

#### 2.6. General procedures for the Heck reaction

In an oven dried round bottomed flask a mixture containing styrene (2.5 mmol), aryl halide (2.5 mmol), the palladium complex  $[Pd(OL^1)]_4$  (0.005 mmol) and potassium carbonate (10.0 mmol) in methanol (10 cm<sup>3</sup>) was heated to reflux for 4 h, as mentioned in Table 3. After the reaction was completed, the solvent was evaporated and the reaction mixture was extracted with diethyl ether. The ether solution was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The ether solution, containing the reaction mixture, was passed through a 12.48 cm silica column (60–120 mesh), the complex was not separated out and it remained trapped in the column. After he desired compound was extracted from the column, the complex was eluted using dichloromethane. Upon evaporation of the ether, solids of the pure products were obtained. The yields of the products obtained from all the reactions were determined after isolation, and the products were characterized by <sup>1</sup>H NMR spectra.

#### 2.7. Crystallography

A single crystal of  $[Pd(OL^1)]_4$  was grown by slow diffusion of petroleum ether into a dichloromethane solution at 298 K. Data were collected by the  $\omega$ -scan technique on a Bruker Smart CCD diffractometer with Mo K $\alpha$  radiation, monochromated by graphite crystal. Structure solution was done by the direct method with the sHELXS-97 program [58–59]. Full matrix least square refinements on  $F^2$  were performed using the sHELXL-97 program [58– 59]. All non-hydrogen atoms were refined anisotropically using reflections  $I > 2\sigma(I)$ . All hydrogens were included in calculated positions. The data collection parameters and relevant crystal data are collected in Table 1.

#### 3. Results and discussion

#### 3.1. Syntheses

The reaction of 2-(2-aminoarylazo)phenol with benzyl bromide in the presence of pyridine and a catalytic amount of KI in dry acetonitrile afforded a reddish yellow mass, from which the orange colored N-benzylated product H<sub>2</sub>OL, **2**, was separated and isolated by preparative TLC. The relevant chemical equation and compounds prepared are shown in Eq. (1).

T-1-1-	-
I DINIE	
Tapic	

Chemical formula	C80.20H64.20N12O4Pd4
Formula weight	1685.64
Crystal system	triclinic
Space group	ΡĪ
a (Å)	14.8428(2)
b (Å)	14.8930(2)
c (Å)	17.4782(3)
α (°)	93.0960(10)
β (°)	110.7710(10)
γ(°)	98.7860(10)
λ (Å)	0.71073
$V(Å^3)$	3545.57(9)
F(000)	952
Ζ	2
T (K)	295(2)
$D (mg/m^{-3})$	1.579
$\mu$ (mm <sup>-1</sup> )	1.059
R <sub>1</sub> (all data)	0.0486
$wR_2[I > 2\sigma(I)]$	0.1118
Goodness-of-fit	1.065



All the  $H_2OL$ , **2**, ligands, were characterized by the usual spectroscopic methods. The purified ligands were used for the reactions with  $Na_2PdCl_4$ . Upon reaction with  $Na_2PdCl_4$  the  $H_2OL$  ligands afforded a dark colored compound as the major product. The compositions of these compounds corresponded to "[Pd(OL)]", according to spectral and analytical data. Interestingly, the "[Pd(OL)]" compounds were actually tetranuclear complexes having the composition  $[Pd(OL)]_4$ , as determined by X-ray studies (see below).



#### 3.2. Spectral characterization and solution structures

The H<sub>2</sub>OL ligands displayed characteristic UV–Vis spectra with absorption maxima near 478 and 325 nm, whereas the violet solutions of the  $[Pd(OL)]_4$  complexes in dichloromethane exhibited characteristic low energy absorption maxima near 555 and 422 nm. Representative UV–Vis spectra of the H<sub>2</sub>OL<sup>1</sup> ligand and  $[Pd(OL^1)]_4$  complex are given in Fig. 1. Relevant data are collected in Section 3.

In the IR spectra,  $v_{OH}$  and  $v_{NH}$  appeared near ~3283 and ~3030 cm<sup>-1</sup>, respectively, and these bands are absent in the complexes [12–15,56,57,60]. The  $v_{N=N}$  band of the H<sub>2</sub>OL ligands (~1460 cm<sup>-1</sup>) was shifted to lower frequency (~1337 cm<sup>-1</sup>) after





Fig. 2. Molecular structure of [Pd(OL<sup>1</sup>)]<sub>4</sub> with the atom numbering scheme. Hydrogen atoms are omitted for clarity.

formation of the Pd(II) complexes, which is consistent with coordination of the azo nitrogen [12–15,56,57,60].

The compositions of the ligands H<sub>2</sub>OL and the corresponding palladium complexes matched well with the C, H, N analytical data and <sup>1</sup>H NMR spectral data. The <sup>1</sup>H NMR data are given in Section 3. The H<sub>2</sub>OL ligands exhibited a sharp singlet at  $\delta$  13.00 ppm for the phenolic OH group [58–60]. The N–H signals (near  $\delta$  9.5 ppm) appeared as broad signals with a triplet-like structure due to coupling with two benzyl protons [12]. This N-H resonance is absent in the <sup>1</sup>H NMR spectra of the complexes, signifying the dissociation of this proton upon complexation [12,14–15]. The methylene proton resonances of the H<sub>2</sub>OL ligands appeared as doublet near  $\delta$  4.59 (5.6 Hz) due to the coupling with the adjacent -NH proton. This doublet for two equivalent of protons split into two sets of doublets each for one equivalent proton near  $\delta$  4.80 and  $\delta$  3.15 in the spectra of the  $[Pd(OL)]_4$  complexes due to the non-equivalent shielding of the two methylene protons. The methyl signal of  $H_2OL^2$  was observed at  $\delta$  2.35. The aromatic proton resonances appeared in the region  $\delta$  8.04 to 6.35 for the ligands and  $\delta$  7.60 to 4.79 for the complexes. All the NMR data above are consistent with the molecular structures obtained from the X-ray studies (see below).

#### 3.3. X-ray structure determination of 3a

Suitable crystals of  $[Pd(OL^1)]_4$ , were grown by slow diffusion of a dichloromethane solution into petroleum ether. A perspective view of the molecule is shown in Fig. 2 and selected bond distances and angles are collected in Table 2. The X-ray structure shows that the composition of the molecule is  $[(OL)Pd]_4$ , where the four palladium atoms are held together by bridging phenolic oxygen atoms. The geometry about each palladium is distorted square planar. The amido and azo nitrogens bind each palladium centre from each of the four dianionic  $OL^1$  ligands.

Table 2
Selected bond distances (Å) and angles (°) for the compound $[Pd(OL^1)]_{4}$

	.,,		
Distances			
Pd(1)-N(1)	1.933(5)	Pd(1)-N(3)	1.970(3)
Pd(1)-O(1)	2.060(3)	Pd(1) - O(2)	2.107(3)
O(1) - C(1)	1.360(5)	N(1)-N(2)	1.278(6)
N(1)-C(6)	1.419(6)	C(1)-C(2)	1.383(7)
N(2)-C(7)	1.337(6)	N(3)-C(12)	1.339(7)
C(2) - C(3)	1.343(9)	C(3) - C(4)	1.369(8)
C(4) - C(5)	1.391(7)	C(5)-C(6)	1.387(8)
Angles			
N(1) - Pd(1) - N(3)	92.06(17)	N(1)-Pd(1)-O(1)	83.42(13)
N(3)-Pd(1)-O(1)	175.26(16)	N(1)-Pd(1)-O(2)	171.55(13)
N(2)-N(1)-C(6)	117.3(4)	N(2)-N(1)-Pd(1)	130.4(3)
C(6) - N(1) - Pd(1)	112.3(3)	N(1)-N(2)-C(7)	122.5(4)
C(12)-N(3)-Pd(1)	124.2(3)	O(1)-C(1)-C(2)	122.2(5)
O(1)-C(1)-C(6)	118.3(4)	C(2)-C(1)-C(6)	119.5(5)
C(1)-C(2)-C(3)	120.0(5)	C(4)-C(3)-C(2)	122.1(5)
N(2)-C(7)-C(12)	127.7(5)	N(2)-C(7)-C(8)	112.9(4)
N(2)-C(7)-C(8)	112.9(4)	C(12)-C(7)-C(8)	119.4(4)

The remaining two coordination sites on each palladium are coordinated by two bridging phenolato oxygens. Thus each palladium is within an (O, O, N, N) coordination sphere. A portion of the molecular structure containing four Pd and four bridging phenolic O atoms and eight coordinated N atoms is shown in Fig. 3.

## 3.4. Catalytic reactions (C–C coupling): Suzuki cross-coupling and Heck reactions

Suzuki cross-coupling and Heck coupling reactions can be represented as given in Scheme 1. Quite a large number of catalysts based on palladium metal and palladium complexes have been



X=IorBr

Scheme 1. Suzuki and Heck reactions.

developed for such reactions [19–53]. Since the advantages of using polynuclear complexes are yet to be identified, we contemplated examining the activity of a new palladium complex,  $[Pd(OL^1)]_4$ , as a catalyst for Suzuki and Heck reactions in THF solvent (Eqs. (3) and (4)).



All the Suzuki reactions, by coupling arylhalides and phenylboronic acid, occurred in refluxing THF ( $\sim$ 66 °C) using K<sub>2</sub>CO<sub>3</sub> as a base, keeping the reaction time constant, i.e., two hours in all cases. The isolated yields and results are collected in Table 3. All the reactions were carried out under a non-inert atmosphere.

Further, we examined the amount of unchanged  $[Pd(OL^1)]_4$  catalyst after the reaction was stopped (after two hours). Spectrophotometrically ( $\lambda_{max} = 556$  nm) we could recognize that 68% of  $[Pd(OL^1)]_4$  remained unchanged. Though this observation did not provide any clue to differentiate between a Pd(0)–Pd(II) and Pd(II)–Pd(IV) mechanism, the issue of a Pd(II)–Pd(IV) cycle could not be discarded [45]. Moreover, the observation did not indicate any particular advantage on using the polynuclear palladium complex as a catalyst. More experimental data are necessary to come to a definite conclusion in this regard.

Heck coupling is another important palladium catalyzed C–C coupling reaction where the substrates are arylhalides (bromoaryls

#### Table 3

Suzuki cross coupling reaction with the catalyst [Pd(OL<sup>1</sup>)]<sub>4</sub>.<sup>a,b,c</sup>

Aryl halide	Product	Isolated yield
I		95
	$\sum - \sum$	92
		90
		87
Br		88
Br		85

<sup>a</sup> Solvent, THF.

<sup>b</sup> Base, K<sub>2</sub>CO<sub>3</sub>.

<sup>c</sup> Time, 2 h.

and iodoaryls) and styrene [42–53]. We have studied the catalytic activity of  $[Pd(OL^1)]_4$  toward conversions of arylhalides to the corresponding stilbene by Heck coupling reactions in refluxing methanol and in the presence of  $K_2CO_3$  (Eq. (4)). The results are given in Table 4. All the reactions were carried out under ambient conditions. Although the catalysis occurred smoothly, at the end of each reaction the  $[Pd(OL^1)]_4$  catalyst could not be isolated as

Table 4	
Heck reaction with the catalyst $[Pd(OL^1)]_4$ . <sup>a,b,</sup>	c

Aryl halide	Product	Isolated yield
		91
		88
O <sub>2</sub> N	O <sub>2</sub> N	85
		90
Br		82
Br		80

<sup>a</sup> Solvent, MeOH.

<sup>b</sup> Base, K<sub>2</sub>CO<sub>3</sub>.

<sup>c</sup> Time, 2 h.

such, signifying that the catalyst may be actually a precatalyst in these reactions. The yields of the products obtained from all the reactions were determined after isolation and they were characterized by <sup>1</sup>H NMR spectra.

#### 4. Conclusion

The synthesis, characterization and structure of new tetranuclear chelates of Pd(II) incorporating the new ligand system H<sub>2</sub>OL have been described. The new N, N, O donor ligands form the tetranuclear assembly through the bridging phenolato oxygen atom. The new  $[Pd(OL^1)]_4$  complex has been used as a catalyst for Suzuki and Heck coupling reactions. The results did not indicate any particular advantage of using the polynuclear palladium complex as a catalyst. More experimental data are necessary to propose a definite conclusion in this regard.

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#### Appendix A. Supplementary data

CCDC 935349 contains the supplementary crystallographic data for [Pd(OL<sup>1</sup>)]<sub>4</sub>. 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: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.07.020.

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