

Design, synthesis and properties of orthopalladated complexes: Proheterogeneous catalyst



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ABSTRACT

The reaction of multidentate ligand, 3-((E)-(2-((E)-4-aryldiazenyl)phenylimino)methyl)benzene-1,2-diol, H₂L (H₂L¹, **1a**; H₂L², **1b** and H₂L³, **1c**) and (E)-2-((2-((E)-4-aryldiazenyl)phenylamino)methyl)phenol, HA (HA¹, **3a**; HA², **3b** and HA³, **3c**) [where H represents the dissociable protons upon complexation, and aryl groups of H₂L and HA are phenyl for H₂L¹ and HA¹, *p*-methylphenyl for H₂L² and HA², and *p*-chlorophenyl for H₂L³ and HA³], with Na₂PdCl₄ separately afforded orthometallated complexes [(L)Pd], (**2a**, **2b** and **2c**) and [(A)PdCl] (**4a**, **4b** and **4c**) respectively. In the case of [(L)Pd], the deprotonated L²⁻ ligands bind palladium (II) in a tetradentate (C,N,N,O) fashion whereas in the case of [(A)PdCl], the deprotonated A⁻ ligands bind Pd(II) in tridentate (C,N,N) manner. X-ray structures of [(L¹)Pd], (**2a**) and [(A¹)PdCl] (**4a**) were determined to confirm the molecular structures. Both the complexes **4a** and **5a** exhibited catalytic activity toward Suzuki and Heck reactions. Conversion of [(A)PdCl] to its oxidized form upon ligand oxidation is reported.

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1. Introduction

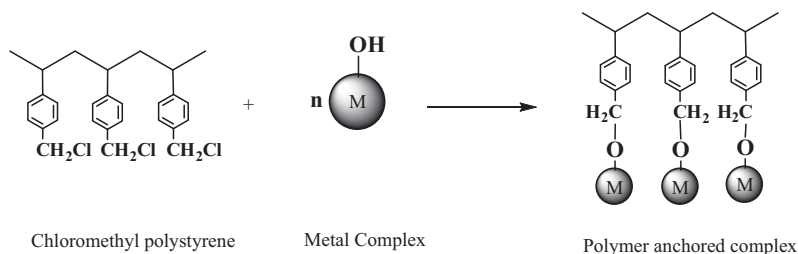
Catalytic activities of organometallic palladium (II) complexes, incorporating azo ligands, in homogenous media have been reported [1–4]. Immobilization of such complexes on solid support is scarce in the chemical literature [5]. Immobilization of potential catalysts on solid support provides the scope to carry out the catalytic process in heterogeneous media. Several strategies have been adopted to anchor the catalyst on solid support [6–18]. Anchoring the catalyst on solid support through covalent linkage is one of the strategies to develop heterogeneous catalysts [6–18].

Synthesis of appropriately designed new palladium complexes possessing catalytic activity in homogenous media and suitable for anchoring on polymer support through covalent linkage is

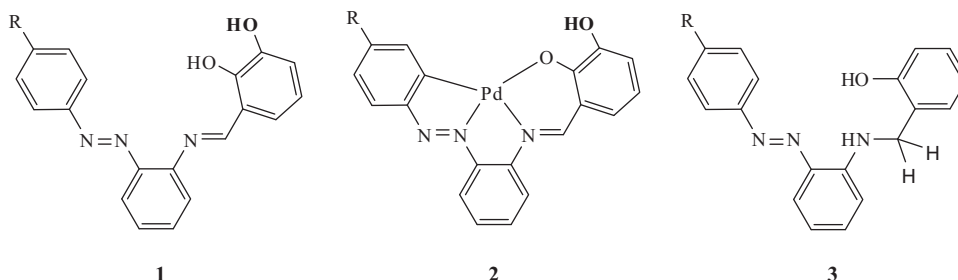
one of the interesting area in current chemical research [1–4]. The notable example involving the condensation of free phenolic –OH, a spectator functional group in the ligand backbone, with the C–Cl fragment on the solid support is one among several strategies employed for affixing the metal complexes on solid polymer support (Scheme 1) [19]. Thus synthesis of metal complexes with free spectator –OH functional group in the ligand backbone and examination of catalytic properties of the complexes in homogenous media are of interest before anchoring. Therefore, we contemplated to design ligands where one free spectator phenolic –OH functional group would be present. Thus we designed the ligand system **1** with the expectation to obtain palladium complexes, **2**. Further, the ligands **3** were used for the synthesis of palladium complexes with a free phenolic –OH functional group.

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Scheme 1.



Herein, we report synthesis of two types of palladium complexes with free phenolic –OH function. Suitability and catalytic activities of the newly synthesized complexes in homogeneous media have been described.

2. Experimental

2.1. Materials

2-(Aryldiazenyl)anilines were prepared according to the reported procedure [20–22]. The solvents used in the reactions were of reagent grade (E. Merck, Kolkata, India) and were purified and dried by reported procedure [23]. 2,3-Dihydroxybenzaldehyde was purchased from Sigma Aldrich and used without further purification. Palladium chloride, sodium borohydride, potassium carbonate, NaBH₄ and silica for thin layer chromatography were purchased from E. Merck, Kolkata, India. Na₂[PdCl₄] was prepared following a reported procedure [24]. Phenylboronic acid, iodobenzene, Styrene, 3-chloro per benzoic acid 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 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 Bruker 400 spectrometers in CDCl₃ and [D₆]-DMSO. Mass spectra were obtained on Waters XEVO G2-S QTOF mass spectrometer.

2.3. Synthesis of ligands H₂L, **1**

All the ligands, **1a**, **1b** and **1c** were prepared following similar procedures. A representative procedure for **1a** is given below.

2.3.1. **1a**

A mixture of 2-(phenylazo)aniline (1.97 g, 10 mmol) and 2,3-dihydroxybenzaldehyde (1.38 g, 10 mmol) in 100 cm³ dry diethyl ether was refluxed for 12 h. A red crystalline solid of **1a** was

obtained after evaporation of the solvent. Isolated yield: 2.54 g (80%). Anal. calc. C₁₉H₁₅N₃O₂ (317): C, 71.92; H, 4.73; N, 13.25. Found: C, 71.63; H, 4.82; N, 13.35%. UV-Vis spectrum (CH₂Cl₂) λ_{max} (ε, M⁻¹ cm⁻¹) = 340 (15869), 300 (28668). IR (KBr pellets, cm⁻¹): ν = 1461 (N=N), 1626 (C=N), 3468 (O–H). ¹H NMR CDCl₃: δ 14.61 (s, OH), 8.64 (s, CH=N), 8.04 (d, 2H), 7.84 (d, 1H), 7.58–7.46 (m, 5H), 7.02 (d, 1H), 6.94 (d, 1H), 6.76 (t, 1H), 6.06 (s, 1H).

2.3.2. H₂L², **1b** and H₂L³, **1c**

Ligands **1b** and **1c** were prepared using 2-(p-tolylazo)aniline and 2-(p-chlorophenylazo) aniline in place of 2-(phenylazo)aniline, respectively. Yield: **1b**, 82% and **1c**, 78%.

Anal. calc. C₂₀H₁₈N₃O₂ (331): Isolated yield: 2.71 g (82%). C, 72.50; H, 5.44; N, 12.69. Found: C, 72.53; H, 5.42; N, 12.75%. UV-Vis spectrum (CH₂Cl₂) λ_{max} (ε, M⁻¹ cm⁻¹) = 327 (14629), 299 (28305). IR (KBr pellets, cm⁻¹): ν = 1454 (N=N), 1616 (C=N), 3407 (O–H). ¹H NMR CDCl₃: δ 14.7 (s, OH), 8.59 (s, CH=N), 7.93 (d, 2H), 7.81 (d, 1H), 7.50 (t, 1H), 7.44 (d, 1H), 7.37–7.31 (m, 3H), 7.00 (d, 1H), 6.90 (d, 1H), 6.73 (t, 1H), 6.16 (s, 1H), 2.43 (t, 3H).

C₁₉H₁₄N₃O₂Cl (351.5): Isolated yield: 2.74 g (78%). Anal. Calc. C, 64.86; H, 3.98; N, 11.95. Found: C, 64.79; H, 3.95; N, 11.99%. UV-Vis spectrum (CH₂Cl₂) λ_{max} (ε, M⁻¹ cm⁻¹) = 356 (18825), 304 (32650). IR (KBr pellets, cm⁻¹): ν = 1454 (N=N), 1626 (C=N), 3411 (O–H). ¹H NMR CDCl₃: δ 14.65 (s, OH), 8.60 (s, CH=N), 7.96 (d, 2H), 7.80 (d, 1H), 7.56 (t, 1H), 7.49–7.44 (m, 3H), 7.34 (t, 1H), 7.03 (d, 1H), 6.92 (d, 1H), 6.75 (t, 1H), 6.16 (s, 1H).

2.4. Synthesis of ligands HA, **3**

The ligands HA², **3b** and HA³, **3c** were prepared following same procedure as reported earlier for **3a** [25] using 2-(p-tolylazo)aniline and 2-(p-chlorophenylazo) aniline in place of 2-(phenylazo)aniline respectively.

2.4.1. HA², **3b** and HA³, **3c**

Anal. Calc. C₂₀H₁₉N₃O (317): Isolated yield: 0.448 g (85%). C, 75.71; H, 5.99; N, 13.25. Found: C, 75.68; H, 5.95; N, 13.13%. UV-Vis spectrum (CH₂Cl₂) λ_{max} (ε, M⁻¹ cm⁻¹) = 450 (2930), 326 (6500), 229 (6745). IR (KBr pellets, cm⁻¹): ν = 1453 (N=N), 3400 (OH). ¹H NMR CDCl₃: δ 7.88 (s, NH), 7.75 (d, 1H), 7.63 (d, 2H), 7.24–7.13 (m, 4H), 7.00–6.81 (m, 3H), 4.50 (d, 2H), 2.34 (s, 3H).

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