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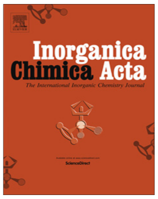

Ruthenium and palladium complexes incorporating amino-azo-phenol ligands: Synthesis, characterization, structure and reactivity

Poulami Pattanayak [a], Sankar Prasad Parua [a], Debprasad Patra [b], C.-K. Lai [c], Paula Brandão [d], Vitor Felix [d], Surajit Chattopadhyay [a,*]

[a] Department of Chemistry, University of Kalyani, Kalyani 741235, India
[b] Department of Chemistry, East Calcutta Girls' College, Kolkata 700089, India
[c] Department of Chemistry, Central National University, Jhong-Li 32001,Taiwan
[d] Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

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ABSTRACT

The ligands 2-((2-aminophenyl)diazenyl)phenol, $HOL^1\text{-}NH_2$, **1a**; 2-((2-aminophenyl)diazenyl)-5-methylphenol, $HOL^2\text{-}NH_2$, **1b**; and 2-((2-aminophenyl) diazenyl)-5-chlorophenol, $HOL^3\text{-}NH_2$, **1c**, which are abbreviated as $HOL\text{-}NH_2$, **1**, afforded the complexes of compositions $[(OL\text{-}NH)Pd(PPh_3)]$, **2**, and $[(OL\text{-}NH)Ru(CO)(PPh_3)_2]$, **3**, upon reaction with Na_2PdCl_4 and $Ru(CO)_3(PPh_3)_3$ respectively. In all the complexes the metals ions, Pd(II) or Ru(II), are coordinated by deprotonated ligand $(OL\text{-}NH)^{2-}$ in tridentate (N, N, O) fashion. X-ray structures of $[(OL^2\text{-}NH)Pd(PPh_3)]$, **2b**, and $[(OL^1\text{-}NH)Ru(CO)(PPh_3)_2]$, **3a**, were determined to confirm the molecular structures. The cyclic voltammograms of $[(OL\text{-}NH)Ru(CO)(PPh_3)_2]$ exhibited two quasi reversible oxidative response near 0.25 and 1.12 V vs. SCE. The nature of HOMO as obtained by DFT calculations has been inspected to have an insight into the redox orbitals. The newly synthesized $[(OL\text{-}NH)Pd(PPh_3)]$, **2a**, complexes exhibited catalytic activity toward the Suzuki, Heck, Cyanation and amination reactions. Catalytic activity of complex $[(OL^1\text{-}NH)Ru(CO)(PPh_3)_2]$, **3a**, was examined for the conversion of ketones to corresponding alcohols by transfer hydrogen reactions.

1. Introduction

Chemistry of platinum metal complexes with azo ligands has been continuing and has drawn considerable interest [1–15]. Several notable results concerning electron transfer reactions [1–8], metal–carbon bond formation [11–13], CH activation [11–13], aromatic ring amination [4], aromatic hydroxylation [11], isomerism [5], cytotoxic properties toward cancer cells and catalytic transformations have been reported [9,10]. The fascinating chemistry of ruthenium and palladium complexes of the ligands, as shown in Chart 1, have been reported. [5,16–22]. Viewing the intriguing chemistry of platinum metals incorporating bidentate phenyl azopyridine (N, N) and azobenzene (N, C) ligands, researchers designed and synthesized several azobenzene based tridentate ligands, such as, arylazophenol (C, N, N) and pyridylazonapthol (N, N, O) ligands, **AB** (Chart 1) [5,7,14,15,17,23,24].

Also, the tridentate (C, N, N or N, N, N) coordination of arylazoaniline and related ligands (**C–G** in Chart 1) to the transition metal ions have been reported [5,10,12,19,20]. Under this milieu, we contemplated to study the chemistry of palladium and ruthenium of amino-azo-phenol ligand, $HOL\text{-}NH_2$, **1**, for the first time where the azo ligands are expected to bind the metal ions in tridentate (N, N, O donor) mode. The complexes of platinum metals of second transition series, Rh, Ru and Pd in particular, have drawn much attention to the chemical researchers because of their catalytic efficiency [25–27]. Since, Ru and Pd substrates are less expensive compared to other higher platinum metals so we contemplated to study the coordination chemistry and catalytic activities of newly synthesized Ru and Pd complexes. In General, Pd(0) and Pd(II) complexes have utilized as catalyst for several kinds of catalytic transformations, e.g., C–C coupling, amination and cyanation [28–37]. Whereas Ru(II) catalysts are well known since the discovery of homogenous hydrogenation [38]. Homogenous reduction of ketones to 2° alcohols by transfer hydrogen catalysis has been considered as one of the convenient processes [39–43]. Therefore we expected interesting results in terms of catalytic activity of newly synthesized platinum metal complexes.

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* Corresponding author.
E-mail address: scha8@rediffmail.com (S. Chattopadhyay).

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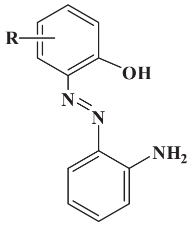

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Herein we describe the syntheses, characterizations and structures of new palladium (II) and ruthenium (II) complexes incorporating tridentate (N, N, O) amino-azo-phenolato ligands, HOL-NH_2, **1**. Catalytic properties of newly prepared palladium complexes toward C–C coupling, cyanation and C–N coupling reactions have been examined and described in this paper. The transfer hydrogen catalysis by newly synthesized ruthenium complexes have been reported in this paper.

2. Experimental

2.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by reported procedure [44]. 2-((2-aminophenyl)azo)phenol, HOL-NH_2 were prepared according to the reported procedure [9,12] Palladium chloride was purchased from E. Merck, Kolkata, India. $Na_2[PdCl_4]$ was prepared following a reported procedure [45]. $Ru(CO)_3(PPh_3)_2$ was prepared was prepared following the reported procedure [46]. Phenylboronic acid, 4-chloro phenyl boronic acid, iodobenzene, bromobenzene, 1-iodo-3,5-dimethylbenzene, 1-iodo-3,4-dimethylbenzene, 1-iodo-2-nitrobenzene, 1-iodo-3-nitrobenzene, 1-bromo-3,5-dimethylbenzene, 1-bromo-2-nitrobenzene, styrene were purchased from Aldrich. $K_4Fe(CN)_6$, triethyl amine, acetophenone, benzophenone, 2-chloro acetophenone, 4-chloro acetophenone, 4-methyl acetophenone were purchased from E. Merck, Kolkata, India. Potassium tertiary butoxide were purchased from Spectrochem, India.

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 $CDCl_3$.

2.3. Synthesis of $[(OL\text{-}NH)Pd(PPh_3)]$, **2**

All the complexes, $[(OL^1\text{-}NH)Pd(PPh_3)]$, $[(OL^2\text{-}NH)Pd(PPh_3)]$ and $[(OL^3\text{-}NH)Pd(PPh_3)]$ were prepared following similar procedures. A representative procedure for $[(OL^1\text{-}NH)Pd(PPh_3)]$ is given below.

2.3.1. $[(OL^1\text{-}NH)Pd(PPh_3)]$, **2a**

A solution of $HOL^1\text{-}NH_2$ (0.100 g, 0.469 mmol) in 15 mL methanol was added dropwise to a solution of Na_2PdCl_4 (0.138 g, 0.469 mmol) in 5 mL methanol. Immediately the color of the solution changed to brown. The mixture was stirred for 8 h at 50 °C. The solvent was evaporated to obtain dark brown gummy mass. The mass was collected and dried under vacuum. This gummy mass was dissolved in dichloromethane (20 ml) and solid triphenyl phosphine (0.120 g, 0.469 mmol) was added. The mixture was stirred for 30 min. Resulting solution was subjected to column chromatography using silica gel (60–120 mesh) and product was separated as a pink band by petroleum ether/ toluene (1:1v/v) mixed solvent as eluent. Upon evaporation of the solvent, the pure $[(OL^1\text{-}NH)Pd(PPh_3)]$ complex was obtained as dark solid. Yield: 60%. $C_{30}H_{23}N_3OPPd$ (565): *Anal.* Calc. for C, 62.07; H, 4.13; N, 7.24.; Found: C, 62.00; H, 4.10; N, 7.30%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 554 (7460), 525 (6020), 445 (4690), 335 (3530), 269 (15560), 225(67200). IR data (KBr, cm^{-1}): ν = 3346 (NH), 1339 (N=N), 1610 (C=N). ^1H NMR $CDCl_3$ (δ, ppm): 8.43 (d, 1H, J = 12.0), 7.98 (d, 1H, J = 8.0), 7.88–7.83 (m, 5H), 7.58–7.48 (m, 10H), 7.31 (d, 2H, J = 2.0), 7.22–7.21 (d, 1H, J = 1.6), 7.06 (t, 1H), 6.67 (t, 1H, J = 8.0), 6.37 (d,1H, J = 8.4) 4.32 (d,1H,NH, J = 8.0).

2.3.2. $[(OL^2\text{-}NH)Pd(PPh_3)]$, 2b and $[(OL^3\text{-}NH)Pd(PPh_3)]$, **2c**

Complexes $[(OL^2\text{-}NH)Pd(PPh_3)]$ and $[(OL^3\text{-}NH)Pd(PPh_3)]$ were prepared using H_2L^2-OH and H_2L^3-OH in place of H_2L^1-OH, respectively. Yield: $[(OL^2\text{-}NH)Pd(PPh_3)]$ 55% and $[(OL^3\text{-}NH)Pd(PPh_3)]$ 50%.

$C_{31}H_{26}N_3OPPd$ (593.94): *Anal.* Calc. for C, 62.63; H, 4.37; N, 7.07. Found: C, 62.65; H, 4.40; N, 7.02%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 554 (12000), 525 (10600), 445 (6515), 335 (6740), 269 (23240), 225 (54000). IR data (KBr, cm^{-1}): ν = 3345 (NH), 1348 (N=N), 1611 (C=N). ^1H NMR $CDCl_3$ (δ, ppm): 8.26 (d, 1H, J = 8.0), 7.96 (d, 1H, J = 12.0), 7.87–7.82 (m, 5H), 7.57–7.48 (m, 10H), 7.04 (t, 2H, J = 8.0), 6.66–6.61 (m, 3H), 6.36 (d, 1H, J = 8.0), 4.73 (d,1H, J = 12.0), 2.36 (s, 3H).

$C_{30}H_{22}N_3OPPdCl$ (593.5): *Anal.* Calc. for C, 58.58; H, 3.74; N, 6.83. Found: C, 58.60; H, 3.70; N, 6.89%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 554 (10000), 525 (8700), 445 (6920), 335 (4980), 269 (21300), 225 (95700). IR data (KBr, cm^{-1}): ν = 3341 (NH), 1344 (N=N), 1611 (C=N). ^1H NMR $CDCl_3$ (δ, ppm): 8.29 (d, 1H, J = 8.0), 7.94 (d, 1H, J = 8.0), 7.84–7.79 (m, 5H), 7.69–7.46 (m, 9H), 7.19 (d, 1H, J = 4.0), 7.07 (t, 1H, J = 8.0), 6.76 (d, 1H), 6.67 (t, 1H), 6.37 (d, 1H, J = 8.0), 4.90 (d,1H, J = 12.0).

2.4. Synthesis of $[(OL\text{-}NH)Ru(CO)(PPh_3)_2]$, **3**

2.4.1. $[(OL^1\text{-}NH)Ru(CO)(PPh_3)_2]$, **3a**

To a solution of $Ru(CO)_3(PPh_3)_2$ (0.0156 g, 0.469 mmol) in toluene (40 mL), $HOL^1\text{-}NH_2$ ligand (0.100 g, 0.469 mmol) was added. The mixture was refluxed for 6 h and a dark solution was obtained. The dark solid, obtained upon evaporation of the solvent, was loaded on preparative silica TLC plate. Pure $[(OL^1\text{-}NH)Ru(CO)(PPh_3)_2]$ complex was separated as green band using toluene/acetonitrile (95:5 v/v) mixed solvent as the eluent. The compound was recrystallised from dichloromethane-petroleum ether mixed solvent. Yield: 50%. $C_{49}H_{38}N_3O_2P_2Ru$ (863.83): *Anal.* Calc. for C, 68.06; H, 4.39; N, 4.86. Found: C, 68.10; H, 4.42; N, 4.80%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 660 (8270), 599 (15100), 489 (25000), 256 (93100). IR (KBr): ν = 3363 (NH) 1925 (C=O), 1608 (C=N), 1352 (N=N) cm^{-1}. ^1H NMR $CDCl_3$ (δ, ppm): 7.67 (d, 1H, J = 8.0), 7.51 (t, 1H), 7.46–7.44 (m, 1H), 7.32–7.13 (m, 15H), 6.78 (d, 1H, J = 8.0), 6.68 (t, 1H, J = 8.0), 6.47 (t, 1H, J = 8.0), 6.14 (m, 2H), 5.95(d, 1H, J = 8.0), 4.58 (s, NH). $E_{1/2}$ [V]: 0.28, 1.17.

2.4.2. $[(OL^2\text{-}NH)Ru(CO)(PPh_3)_2]$, **3b** and $O(L^3\text{-}NH)Ru(CO)(PPh_3)_2]$, **3c**

Complex $[(OL^2\text{-}NH)Ru(CO)(PPh_3)_2]$ and $[(OL^3\text{-}NH)Ru(CO)(PPh_3)_2]$ were prepared and purified following a similar procedure as described for $[(OL^1\text{-}NH)Ru(CO)(PPh_3)_2]$ using ligand $HL^2\text{-}NH_2$ and $HL^3\text{-}NH_2$ in place of $HL^1\text{-}NH_2$. Yield: 0.114 g, (60%) and 0.101 g (55%) respectively.

$C_{50}H_{40}N_3O_2P_2Ru$ (877.83): *Anal.* Calc. for C, 68.35; H, 4.55; N, 4.78. Found: C, 68.38; H, 4.59; N, 4.70%. UV–Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 660 (5500), 599 (10000), 489 (21000), 319 (26000), 256 (60000). IR (KBr): ν = 3361 (NH) 1927 (C=O), 1608