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A Study of Palladium (II) Schiff Base Ligand Complexes of Benzofuran and Its Schiff's Bases

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Abstract – The palladium(II), copper(II), cobalt(III) and ruthenium (III) Schiff base complexes with 2-(5,6-Dihydro-benzo[4,5]imidazo[1,2-c]quinazolin-6-yl)- 6-methoxy-phenol (L1), 4-(5,6-Dihydro-benzo[4, 5]imidazo[1,2-c]quinazolin-6-yl)- 2,6-dimethoxy-phenol (L2), 4-Chloro-2-(5,6-dihydro-benzo[4,5]imidazo[1,2-c] quinazolin-6-yl)-phenol (L3) , 4-Bromo-2-(5,6-dihydro-benzo[4,5]imidazo[1,2-c] quinazolin-6-yl)-6-methoxy-phenol (L4), were summarised as dichloromethyl, ethanol/benzene medium, all of which are strong stable, long-term in air, characterised by different physicochemical technologies. The complexes are water insoluble but DMF and DMSO soluble. Yet ethanol and methanol are readily soluble in ruthenium and palladium complexes. The experimental evidence on the complex elemental analysis is well in line with that of the formulation being proposed. The observed molar conductance values are consistent with the non-electrolytic properties of the preparations except for the Co(III) complexes, which are electrolytes, for all the complexes of 10−3 M DMF solution. By analysing different physicochemical techniques, the structures of the prepared complexes are proposed. Palladium (II) complexes are based on experimental results, showing slightly distorted flat geometry with a 1:1 (M:ligand) ratio of all ligands. The complexes [1:2 (M:ligand) and 1:1:1 (M:ligand:phen)] are copper(II), and cobalt(III)], while octaheral geometry is present. The octahedral geometry exhibits for the ruthenium complexes in a 1:1:1 (M: ligand: phen) ratio. The proposed stoichiometry for prepared complexes is verified by thermographometrical studies. In addition, thermographs demonstrate the existence in the complexes studied of the lattice/coordinate water molecules. The experimental weight losses, which lead to the successive degradation of metal complexes, are very much in line with the values measured. The last step is the formation of oxides such as PdO, CuO, CoO and Ru2O3. The decomposition is completed. The single crystal structure of 3a was analysed in detail, a palladium-Schiff base complex. However the single production of crystal was not successful for the remaining complexes.

Key Words – Palladium (II), Schiff Base Ligand, Benzofuran, Physicochemical Techniques

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INTRODUCTION

Palladium is one of the most widely used metal both in laboratory and in industry [1]. It finds applications in catalysis viz., hydrogenation [2], carbon-carbon and carbon-oxygen bond formation [3], catalytic oxidation to carbonyl compounds and oligomerization of alkenes, alkynes and dienes as well [4]. Coordinatively unsaturated with lower oxidation states of palladium complexes are expected to show high and characteristic relativities for both coordinative and oxidative addition reaction which are very important steps in a catalytic cycle [5]. The lower oxidation states of such complexes are stabilized by electron rich and sterically bulky ligands.[6]

Schiff base ligands are serving as the best in terms of their coordinating ability with most of the transition metals [7]. They act as a scaffold for the synthesis of coordination compounds. The synergic mechanism is involved in the formation of coordination bond with Schiff bases. Schiff bases with electron tuning ability can be better at their coordination with transition metals and it is achieved by substituting electron donating groups. Hence, the electron tunable property of Schiff base made them a perfect candidate for the synthesis of coordination compounds.

Palladium Schiff base compounds mediated cross coupling reactions have revolutionized the synthetic organic chemistry. Of all the carbon-carbon coupling reactions Suzuki-Miyaura [8], Heck [9] and Stille [10] reactions are mainly studied. These reactions involve both heterogeneous and homogenous catalysis. In homogenous catalysis both catalyst and reactants are in the same phase, usually liquid. There is a good contact with reactants, so that there is a much greater effective concentration of catalyst than with heterogeneous catalysis. However, in heterogeneous catalysis the effective concentration of catalyst is low, to enhance this, the catalysts are spread thinly on a cheap solid support. Immobilization of transition metal Schiff-base complexes onto zeolite, polymeric or clay matrices has been adopted to prepare heterogeneous catalysts [11]. The use of solid phase support may induce many problems due to heterogeneous reaction conditions. One of the prominent achievements in this field is the use of ionic liquids as homogeneous immobilization of transition metal catalyst in organic synthesis [12]. Ionic liquid (IL) immobilized catalysts can induce organic reactions, and such reactions were carried polar solvents, which results in a homogeneous system. After the completion of the reaction, a non-polar solvent, such as diethyl ether is added and the IL immobilized catalyst can be separated easily from the polar phase due to the difference in their solubility. Consequently, the IL immobilized catalyst is regenerated and can be used for further reactions.

Many biaryls are found in industrial applications, such as drugs, conducting polymers, liquid crystal materials and natural products [13]. The 2010 Nobel Prize in chemistry was awarded to Suzuki for his discovery and development of the Suzuki reaction for biaryls [14]. The development of improved reaction conditions for the Pd-catalyzed Suzuki reaction has received much attention recently [15]. The choice of ligand is known to be crucial to the success of such a catalytic reaction. In this context, benzimidazole-containing ligands have proven to be good candidates for complexation with metals due to their exceptional coordination ability and versatile conformations. Benzimidazole molecule with rigid structure and high electron transfer capability can easily provide nitrogens to coordinate with transitions metals. Palladium-catalyzed C–C coupling reactions with N- donor ligands have been reported much less common is a recyclable and reusable homogeneous catalytic system with benzimidazole Schiff base ligand. There has always been a demand for the development of a robust, efficient and cost effective catalyst that can circumvent the limitations of the existing catalysts. Moreover, environmental concerns and economic considerations also make it essential to develop catalytic systems that can be recovered and recycled, especially when noxious transition metals are involved.

Palladium Schiff base complexes are widely used in many cross coupling reactions. Palladium complexes with N-donor ligands particularly benzimidazole Schiff base complexes are one of the best entities as a ligand, because of their high coordination ability. Benzimidazole Schiff base complexes also exhibit biological activities ranging from antimicrobial to anticancer. Synthesized a series of benzimidazole palladium complexes and systematically characterized by elemental and various spectroscopic techniques. The antibacterial activity of the synthesized compounds were established against both gram positive and gram negative bacteria, the studies suggested that few of the Pd(II) complexes showed moderate to good activity against the bacterial strains under study and also compared to standard streptomycin.

The use of palladium(II) complexes over platinum(II) complexes for anticancer activity is well explored in the recent years, owing to their high hydrolysis of palladium complexes over platinum counterparts. Pd(II) and Pt(II) complexes with N, N'- 1,2-diamino-4-fluoro-5-(4-methyl-1- piperazinyl) benzene (DFMPB) ligand, and these compounds were characterized by spectroscopic methods. The cytotoxicity of the prepared compounds was studied against MDA-231, MCF-7 and K562. The compounds were exhibited dose dependant inhibition in the growth of cell lines, also the Pd(II) complexes showed better results compared to their Pt(II) counterparts and the standard Cisplatin with an IC50 of 63.83, 71.53 and 59.36 μM, respectively.

The interaction of metal complexes with protein has been an area of advanced research in determining the pharmacokinetics and pharmacodynamics in drug delivery and drug metabolism. The metal complexes bind to DNA via electrostatic, covalent and non-covalent pathways. The synthesis of a series of tridentate N, N, N-pyridyl-dioximepalladium(II) complexes and structurally well characterized by various spectroscopic techniques. The interaction of complexes with CT-DNA and BSA has been studied by fluorescence and UV-vis spectroscopic methods. The Pd(II) complexes display intercalative binding to CT-DNA and stronger binding affinity for BSA and HSA.

The catalytic activities of the palladium Schiff base complexes are well explored. The ability of palladium complexes in carbon-carbon cross coupling reactions they were synthesized different N, N, O, O- tetradentate Schiff base palladium complexes. Single crystal studies show that they form square planar complexes. The synthesized Schiff base complexes were then subjected for their catalytic ability in Suzuki and Heck reactions. Since oxidative addition step is the rate determining step in any coupling reaction and the oxidative ability of the palladium metal can be enhanced by the inclusion of electron donating group.

The triphenyl phosphine ligands having both σ-donor and π- acceptor capacity can be used as an auxillary ligand along with Schiff base ligand. Also, it is known that it stabilizing the lower oxidation state of the palladium metal. Synthesized palladium (II) pyridoxalhydrazone Schiff base complexes and structural characterization was detailed. Based on X-ray diffraction study, a distorted square planar geometry was proposed for the Pd(II) complex. The protocol for the Suzuki cross coupling reaction was described to obtain biaryl products in good yield.

Green methodology in the synthesis of biaryls is well established in the recent years; by using green solvents particularly water. The single crystal X-ray study reveals the distorted square planar geometry around the metal ion via nitrogen from imine and imidazole moiety. The catalyst shows good to moderate yield in the synthesis of biaryls from Suzuki cross coupling reaction. The low catalyst loading of the order of 0.1 mol% and water soluble by-products makes the green approach for the synthesis of biaryls.

The complex was well characterized by elemental and various spectroscopic analyses. The ionic liquid tagged Schiff base palladium complex was explored for its utilization in Suzuki reaction. The isolation and reusability of the catalyst are simple and effective since, it can be reused for seven times without much loss in the activity. The use of aqueous solvent, simpler separation techniques and recyclability made the method a greener approach. The yields were good to moderate at very low catalyst load.

Recent review about the developments of Suzuki reactions were covered a detailed literature dated from 2010 to 2015. The review covers all general aspects of carbon – carbon coupling reactions involving organ boron reagent and organic halides or pseudo halides in the presence of palladium and nickel. They have pointed out both heterogeneous and homogenous methods in developing new methodology and with minor modifications in the carbon-carbon forming reactions. The homogenous immobilization of heterogeneous method has been an area of current research accompanied with the use of zeolites, silica supported materials, Nano tubes, tagged ionic liquid and also as solvent.

Apart from the application of palladium(II) complexes in carbon-carbon bond formation reactions, Shilpa and Gayatri have prepared a polymer supported [2-(2'-pyridyl)benzimidazole] palladium complex by functionalizing ligand onto a chloromethylated polystyrene and then reacting it with $PdCl_4$. The polymer supported palladium complex was characterized by physicochemical methods. The catalytic hydrogenation of carbon – carbon double bond was carried out at ambient temperature with good to moderate yield and recyclability up to six times without any leaching of metal content from the polymer support. The catalyst also showed good selectivity for C=C in the presence of -nitro, -CO and -CN groups.

The inclusion of metal in fabricating devices for non-linear optics (NLO) has been an essential criterion, as it induces more sub energy levels for transitions. Rudresha and his coworkers have synthesized Pd(II)-Schiff base complex containing tri phenyl phosphine as an auxiliary ligand, and then the poly(methylmethacrylate) PMMA composites were prepared to check thier utility in NLO devices. The third order ultrafast non linearity was found to be of the order of 3.9 × 10-10 esu estimated by optical kerr gate method. The non-linear absorption coefficient was found to be -23 cm/GW. The study suggested that the palladium complex can be used as a potential ultra-fast photonic device.

Based on the thorough literature and owing to its wide variety of applications ranging from antimicrobial, anticancer, protein binding interactions to catalytic applications in carbon–carbon bond formation reactions. In this chapter, the author has made his interest on the synthesis of palladium benzimidazole Schiff base complexes from 2-(5,6-Dihydro-benzo[4,5]imidazo[1,2-c]quinazolin-6-yl)-6-methoxy-phenol (L1), 4-(5,6-Dihydro-benzo[4,5]imidazo[1,2-c]quinazolin-6-yl)-2, 6-dimethoxy-phenol (L2), 4-Chloro-2-(5,6-dihydro-benzo[4,5]imidazo[1,2- c]quinazolin-6-yl)-phenol (L3), 4-Bromo-2-(5,6-dihydro-benzo[4,5]imidazo[1,2- c]quinazolin-6-yl)-6-methoxy-phenol(L4) via ring opening of benzimidazo [1,2- c]quinazoline by palladium benzonitrile precursor, and their applications in the Suzuki coupling reactions in an ionic liquid as a robust and recyclable catalytic system.

The bases of the Schiff are typically bi-, tri-, and tetra- and polydecent ligands, primarily connected to the aldehyde or amine fragment via the lonely pair in azomethine 'n' along with one or more donor atoms in close proximity to the azomethinic group (Fig. 1). The combination of salicyl aldehydes or their derivatives with aliphatic 1,2diamines will lead to the formation of an extremely important class of ligands called "salen," while with aromatic 2,2 diamine groups lead to the forming of conjugate μ-conjugated atoms (commonly used are nitrogen and oxygen), but oxygen can be substituted with sulphur , nitrogen or selenium atoms. The reaction of aldehydes to monoamines is obtained by bidentsalicylaldimines.

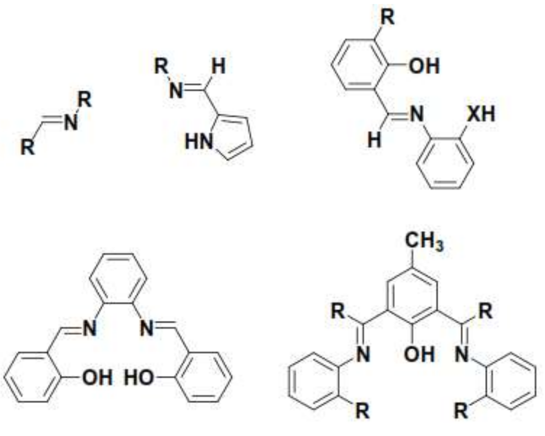

Fig. 1: Examples of Schiff bases of varied denticities

Also of significant research interest have been the macro-cyclic Schiff base ligands (Fig. 2), which encompass ligands that find large applications in macro-cyclic and supramolecular chemicals. In the present research, the ligand systems selected are mainly focused upon bidentsalicylaldin and tetradent saline and salphene forms. Their multisalic nature results in very high binding values of several d or f block-metals. Such ligand systems are considered 'preferable ligands' for their chelating potential in the various oxidation states to chelate a large range of metal ions, including main group, transition, and inner transition metal ions.

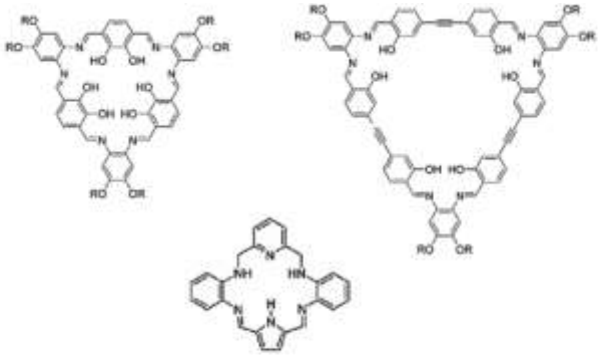

Fig. 2: Examples of macro cyclic Schiff base ligands

SCHIFF BASE LIGANDS

Schiff base is one of the potent organic moieties which can be used for the preparation of metal complexes. The first person to mention Schiff base was Hugo Schiff in 1864, which is a slightly acidic state and the use of dehydration agents. (Figure 3).

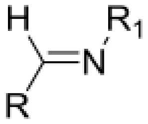

Figure 3: General representation of Schiff base

The heterocyclates can also be replaced with electric donor groups, which help to change bonding and stability of synthesised metal complexes, where R and R1 are alkyl, cycloalkyl, aryl and heterocyclic groupings with the general formulation RHC = N-R1.

The forming process for bases of Schiff was shown in Figure 4, which shows that the acid medium is important for the subsequent Schiff base formation. In the initial stage, acid-like proton, in most cases acetic acid, assaults the carbonyl-compound oxygen, and eventually, a 1, 3-H-shift followed by removal of the water molecule to create the intended compound. However, replacement of reacting molecules, in particular a carbonyl compound retracting electron set and an amine reactant substitute electron may have a significant effect on yield. The production can also be further improved by the elimination of the water by-product from the reaction mixture. The attachment of a good dean with a reaction set-up is able to accomplish this.

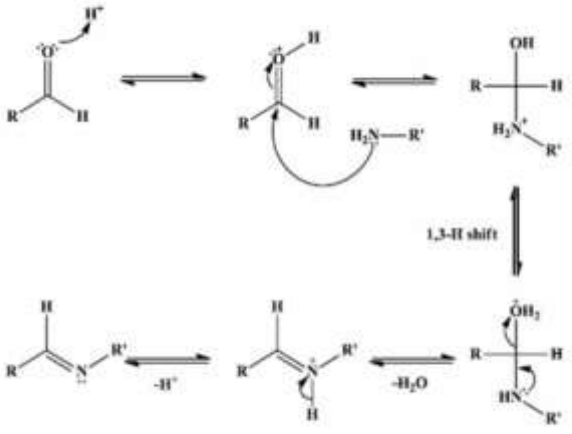

Figure 4: Mechanism of imines formation

In certain cases, tautomerism, intramolecular cycling or rearrangement leading to the formation of analogue Schiff basal derivatives is undertaken during the synthesis of Schiff bases ligands. The derivatives of these Schiffbase function as a ligand to be binding with different metals leading through structural rearrangement to the creation of Schiffbase complexes giving a more organised environment. The Schiff bases are used for the synthesis of heterocyclic compounds apart from its position as ligands. There are few records, however, that the Schiffbases in complex formation are reduced and act as ligands. Metal hydrides can be used to generate the synthesis of earlier products and sodiumborohydride can generate the higher specificity.

CHEMICALS

All reagents, $PdCl_2$ and benzonitrile were procured from Sigma Aldrich Chemicals Pvt. Ltd., Bengaluru and used as received without purification. All other solvents and chemicals were of anal grade.

Preparation of palladium precursor, $[Pd(PhCN)_2Cl_2]$

The above precursor was prepared by stirring a mixture of $PdCl_2$ (0.5g, 2.82 mmol) with 30 mL of benzonitrile until all the $PdCl_2$ dissolves at 100 °C under nitrogen atmosphere to give a clear yellow solution. Addition of the former to 100 mL of petroleum ether at room temperature yielded yellow solid which was filtered and washed with excess of petroleum ether and dried (yield 95%).

Preparation of palladium catalyst $[Pd(L1)Cl]\ H_2O$ [3a]

Palladium catalyst 3a was prepared by stirring a mixture of bis (benzonitrile) palladium(II) chloride with L1 in dichloromethane (MDC) in a 1:1 ratio for

1 h at room temperature under nitrogen atmosphere. Coordination was immediate since there is a change in color from pale yellow to orange color solid formation. The solid was filtered off, washed with MDC and dried in vacuo.

Compound 3a: yield: (73%). m.p 285-287 °C. IR ν (cm-1): 1617 (HC=N), 3320 (NH, benzimidazole), ESI–MS m/z: 503.0450 [M+1]+ . Anal.Calcd.for [C21H18ClN3O3Pd] (%) C, 50.22; H, 3.61; N, 8.37.Found C, 50.11; H, 3.22; N, 8.21. 1H NMR 14.082 (s, NH, 1Himi); 9.369 (s, 1H, -HC=N); 8.597 (d, 1H, J=8.4 Hz, ArH); 8.103 (d,1H,J= 6Hz, ArH); 7.680 (t, 2H, J= 8Hz, ArH); 7.561 (d, 2H, J= 7.6Hz, ArH); 7.360-7.330 (m, 1H, ArH); 7.274-7.190(m, 1H, ArH); 7.135 (d, 1H, J= 8Hz, ArH); 6.900 (d, 1H, J= 7.6Hz ArH); 6.538-6.499(m, 1H, J= 8Hz ArH); 3.766(t, 3H,OCH3). 13C NMR 177.752, 148.414, 147.488, 147.169, 146.775, 146.539, 145.090, 140.506, 133.935, 131.347, 129.989, 127.340, 124.396, 124.168, 123.242,119.448, 118.719, 116.025, 115.859, 111.973, 56.477. Conductance (Λ, Ω-1 cm 2 mol-1): 6.1. μeff (BM): Diamagnetic.

Preparation of palladium catalyst [Pd(L2)Cl2].H2O [3b]

A mixture of bis(benzonitrile)palladium(II) chloride was treated with L2 in MDC in a 1:1 ratio for 1 h at room temperature under nitrogen atmosphere. An intense yellow color solid was obtained instantaneously. The solid was filtered off, washed with MDC and dried in vacuo.

Compound 3b: yield: (70%). m.p 275-279 °C. IR ν (cm-1): 1618 (HC=N), 3322 (NH, benzimidazole), ESI–MS m/z: 551.04 [M+1]+ . Anal.Calcd.for [C22H21Cl2N3O4Pd] (%) C, 46.46; H, 3.72; N, 7.39.Found C, 46.21; H, 3.60; N, 7.20. 1H NMR 14.012 (s, NH, 1Himi); 9.324 (s, 1H, -HC=N); 8.610 (s, 1H, OH); 8.213 (d, 1H, J=8.2 Hz, ArH); 8.085 (d,1H,J= 6.2 Hz, ArH); 7.690 (s, 2H, J= 8Hz, ArH); 7.534 (d, 1H, J= 7.6Hz, ArH); 7.380-7.320 (m, 1H, ArH); 7.234-7.140(m, 1H, ArH); 7.135 (d, 1H, J= 8Hz, ArH); 6.900 (s, 2H, ArH); 6.498; 3.778 (t, 6H, (OCH3)2). 13C NMR 176.123, 148.456, 147.898, 147.111, 146.785, 146.564, 144.890, 140.475, 134.535, 130.567, 129.865, 126.742, 124.654, 124.487, 122.275, 119.444, 118.762, 116.525, 114.744, 110.447, 56.533. Conductance (Λ, Ω-1 cm 2 mol-1): 5.1. μeff (BM): Diamagnetic

Preparation of palladium catalyst [Pd(L3)Cl].H2O [3c]

A coordination compound 3c was prepared by stirring a mixture of bis (benzonitrile)palladium(II) chloride with L3 in MDC in a 1:1 ratio for 1 h at room temperature under nitrogen atmosphere. A pale yellow color of the reaction mixture was changed to brick red color immediately after mixing the reactants to get brick red solid compound. The obtained solid was filtered off, washed with MDC and dried in vacuo.

Compound 3c: yield: (75%). m.p 280-282 °C. IR ν (cm-1): 1614 (HC=N), 3318 (NH, benzimidazole), ESI–MS m/z: 506.93 [M+1]+ . Anal.Calcd.for [C20H15Cl2N3O2Pd] (%) C, 47.41; H, 2.98; N, 8.29.Found C, 46.89; H, 2.52; N, 7.91. 1H NMR 14.015 (s, NH, 1Himi); 9.727 (s, 1H, -HC=N); 8.365 (d, 1H, J=8.2Hz, ArH); 8.103 (d, 1H, J=8.2Hz, ArH); 7.965 (s,1H, ArH); 7.660 (t, 2H, J=8.2Hz, ArH); 7.465 (d, 1H, J=8.0Hz, ArH); 7.354-7.310 (m, 1H, ArH); 7.264-7.175(m, 1H, ArH); 7.120 (d, 1H, J=8.0Hz, ArH); 6.952 (d, 1H, J=7.6Hz ArH); 6.695 (d, 1H, J=8Hz ArH). 13C NMR172.456, 148.424, 147.411, 147.235, 146.756, 146.543, 145.124, 140.456, 133.423, 132.747, 130.471, 128.740, 125.687, 124.175, 123.245, 120.664, 118.754, 116.754, 115.564, 110.564. Conductance (Λ, Ω-1 cm2 mol-1): 5.4, μeff (BM): Diamagnetic

Preparation of palladium catalyst [Pd(L4)Cl] [3d]

A maroon colored solid was obtained by stirring a mixture of bis(benzonitrile)palladium(II) chloride with L4 in MDC in a 1:1 ratio for 1 h at room temperature under nitrogen atmosphere. The solid was filtered off, washed with MDC and dried in vacuo.

Compound 3d: yield: (73%). m.p 275-277 °C. IR ν (cm-1):1617 (HC=N), 3320 (NH,benzimidazole),ESI –MS m/z: 503.0450 [M+1]+ . Anal.Calcd.For[C21H15BrClN3O2Pd] (%) C, 44.79; H, 2.68; N, 7.46. Found C, 44.59; H, 2.42; N,7.18. 1H NMR 14.128 (s, NH, 1Himi); 9.413 (s, -HC=N, 1H); 8.595 (d, 1H, J=8.0 Hz,ArH); 8.122 (d, 2H, J= 8.0 Hz, ArH); 7.703 (t, 2H, J= 5.6 Hz, ArH); 7.619-7.570 (m, 2H, ArH); 7.367-7.330 (m, 1H, ArH); 7.293-7.254 (m, 1H, ArH); 6.963 (s, 1H, ArH); 3.766 (t, 3H,OCH3). 13C NMR 175.226, 161.226, 151.547, 145.371, 143.579, 141.238, 134.803, 133.455, 129.612, 128.531, 127.562, 125.140, 124.954, 124.405, 124.131, 123.283, 121.418, 118.286, 115.509, 112.619, 56.680. Conductance (Λ, Ω1 cm 2 mol-1): 6.0. μeff (BM): Diamagnetic

PHYSICAL MEASUREMENTS

The synthesized palladium complexes were characterized by analytical, physical and spectral techniques.

1. Electrical conductance measurements

The molar conductance data of the isolated complexes were recorded in 10^{-3} M DMSO solution at room temperature using an Elico CM-180 conductometer, with a cell constant of the conductivity cell used was 1 cm^{-1}.

2. Thermal degradation studies

Thermogravimetry is an analytical technique operates by recording the mass of a sample continuously as a function of temperature or time on heating or cooling at a controlled rate. The thermo gram so obtained is capable of giving valued detailsabout the thermal stability of a sample, dependence of mass change and composition of a sample on temperature, the decomposition pattern and the residue left. The thermograms for the complexes were recorded in nitrogen atmosphere on TGA-Q50 instrument keeping the final temperature at 800 °C with the heating rate at 10 °C/min. The calibration of temperature scale of the instrument was done with calcium oxalate ($CaC_2O_4{\cdot}H_2O$).

3. X-ray crystallographic Analysis

The crystals suited for X-ray crystallographic measurements were obtained by slow diffusion of diethyl ether into the solution of the 3a in methanol at room temperature. The crystal was mounted on a glass fiber. X-ray diffraction data of 3a was collected on a Bruker, MicrostarProteum 8 diffract meter at 296 K. Data was collected using Cu-Kα radiation (λ=1.54178 Å) at 296 K with the ψ and ω scan method. The structure of 3a was solved by direct methods using the SHELXS program and all of the non-hydrogen atoms were refined anisotropically by full matrix least square based on F^2 using the SHELXL–program .Hydrogen atoms were placed in calculated positions and included in the refinement using the riding model. The attempts for the development of single crystals of other palladium complexes 3b, 3c and 3d were unsuccessful.

CATALYTIC ACTIVITY

The catalytic efficacy of the prepared complexes 3a, 3b, 3c and 3d in Suzuki reaction was carried out in order to check the suitability of the studied complexes as catalyst. Firstly, the screening was done with respect to the concentration of the catalyst 3a, 3b, 3c and 3d. Later, the best of the above catalyst was optimized for different constraints in Suzuki-Miyaura cross coupling reaction.

1. General procedure for Suzuki coupling reaction

To a 50 mL round bottom flask, aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), 3a-3d (0.1 mol%), K_2CO_3 (2.0 mmol) and (1-Ethyl-3-Methylimidazolium Hexafluorophosphate) EMIM [PF6]-water mixture (1:1, 2 mL) were added, and continuously stirred at room temperature (25 °C). The progress of the reaction was monitored at regular 5 minute interval by TLC. After the completion of the reaction, the crude reaction mixture was diluted with water (20 mL) and extracted with a mixture of hexane and ethyl acetate (1:1 v/v, 3 × 10 mL). Diethyl ether was used for extraction in case of some substrates. The organic layer was dried over anhydrous Na_2SO_4, and then the solvent was removed under reduced pressure. The resulting crude residue was purified by column filled with silica gel (mesh 60–120), using n-hexane–ethyl acetate as an eluent, to give the pure product. The products were analyzed by NMR spectroscopy.

CONCLUSION

The Schiff base complexes of palladium(II), copper(II), cobalt(III) and ruthenium(III) with the above ligands (L1-L4) have been synthesized indichloromethane/ethanol/benzene medium and characterized by various physicochemical techniques, all of these complexes are solids, coloured, and stable to air for longer period. The complexes are water insoluble but they are soluble in DMF and DMSO. However, ruthenium and palladium complexes are easily soluble in ethanol and methanol. The experimental data of elemental analysis of the complexes are in good agreement with that of proposed formula. The observed molar conductance values, for all the complexes at 10−3 M DMF solution are consistent with the non-electrolytic nature of the prepared complexes except for Co(III) complexes, which are electrolytes.The structures of the prepared complexes are proposed, by studying various physicochemical techniques. Based on the experimental data, palladium(II) complexes, exhibits slightly distorted square planar geometry with all the ligands in 1: 1(M:ligand) ratio. Whereas, copper(II) and cobalt(III) complexes [both 1:2 (M:ligand) and 1:1:1 ((M:ligand:phen)] shows an octahedral geometry. For ruthenium complexes in the stoichiometric ratio of 1:1:1 (M:ligand:PPh3), exhibits octahedral geometry. Thermogravimetric studies, confirms the proposed stoichiometry for the prepared complexes. Also, thermograms show, clearly the presence of lattice/coordinate water molecules in the studied complexes. The experimental weight losses, corresponding to the successive degradation of metal complexes are in close agreement with that of the calculated values. The last step of the decomposition leads to the formation of metal oxides as PdO, CuO, CoO and Ru_2O_3. The single crystal structure of 3a; a palladium-Schiff base complex was studied in detail. However, single crystal development for the remaining complexes was unsuccessful.

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