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Synthesis And Characterization of 2-Phenyl-2-benzimidazole, 1,2,4,5-tetraphenyl-imidazole And Its Cycloruthenated (II) Complexes

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Abstract

In the present work, a precursor and ligands were synthesized such as $[Ru(bpy)_2Cl_2].2H_2O$,2-phenyl benzimidazole and tetrasubstituted Imidazole respectively for the production of Cycloruthenated (II) complexes like $[Ru(bpy)_2(2PB\text{-}L)]PF_6$ and $[Ru(bpy)_2(1,2,4,5\text{-}tetraph\text{-}im)]PF_6$. The synthesized compounds have been characterized on the basis of elemental analysis and various spectroscopic studies viz., Infrared spectroscopy (IR); UV-Visible spectroscopy. These complexes have wide range of application such as anticancerous and antimicrobial properties.

Keywords : Cycloruthenated (II) Complexes , 2-phenyl benzimidazole , Tetraphenyl imidazole.

1. Introduction:

Recent research is proceeding towards the enhancement in the properties of ruthenium complexes for their applications in the field of anticancer activity, catalytic property and photophysical and chemical properties. Since couple of years ruthenium complexes is gaining more attention from the researchers because of their various application in life sciences, medicine, catalytic reaction, nanotechnology and many more areas[1-5]. The broad and red-shifted absorption properties of the cyclometalated complexes of ruthenium(II) render these as a new class of promising sensitizers because they are shown to dramatically change the electronic properties by raising the energy of their HOMO[6]. Among the most widely studied complexes, particularly popular are ruthenium complexes derived from bipyridine-type of ligands. Many complexes of this type (such as $[Ru(bpy)_3]^{2+}$, bpy = 2,2′-bipyridine) are of interest because they absorb a significant portion of the visible spectrum, have relatively long-lived excited states (>1 μs), are often stable following one-electron oxidation and reduction, and exhibit good photochemical stability. Various Ru(II) complexes by incorporating bipyridines and thiocyanate ligands have been published to improve the device efficiency and stability[7].

2. Experimental Section:

2.1 Materials and Instruments:

All chemicals used in this work were of analytical grade. $RuCl_3.3H_2O$, 2,2'-bipyridine(bpy),1,10-phenanthroline monohydrate, benzaldehyde, ethylene diamine, KI(potassium iodide), benzil, aniline, ammonium acetate, p-toluene sulphonic acid, potassium carbonate, iodine , potassium hexafluoro phosphate were obtained from S.D. Fine Chemicals Limited (India). The solvents methanol, ethanol, acetonitrile, DMF, DMSO, Chloroform, DCM, acetone, ethyl acetate, hexane and diethyl ether etc. were used of AR Grade.

The ligands and complexes synthesized during the study have been characterized by Nuclear magnetic resonance (NMR) by Varian-Mercury 300 MHz spectrometer, UV-visible absorption measurements were carried on JASCO V-630 Spectrophotometer and Infrared spectroscopy (IR) by Shimadzu FTIR-8400 spectrophotometer at department of the chemistry, University of Pune.

2.2 Synthesis of Ligands :

a) Synthesis of 2-Phenyl-1H-benzimidazole (L1) :

A 25 mL round-bottomed flask was charged with acetonitrile (3 mL), N-benzylbenzene1,2-diamine (1.96 g, 10 mmol), I2 (0.25 g, 1 mmol), TBHP (1.8 g, 20 mmol) and the reaction mixture were stirred at room temperature. After completion of the reaction, the solvent was distilled and the product was purified by column chromatography over silica gel, affording benzimidazole. MP: 289–291 _C (lit. Prokopcova and Kappe (2007) 291–292 _C); pale yellow solid; 1H NMR (400 MHz, DMSO-d6): 7.20 (m, 2H), 7.40–7.62 (m, 5H), 8.20 (d, J= 8.4 Hz, 2H),12.92 (s, 1H) [8].

Fig. 1: Synthetic scheme of L1

b) Synthesis of 1, 2, 4, 5-tetraphenyl-imidazole (L2):

A mixture of benzil (10 mmol) ,ammonium acetate (10 mmol), aniline (10 mmol), aromatic aldehyde (10 mmol), and PTSA (5 mol %) stirred at 80 °C in ethanol (5 ml) for 1 hour . The completion of reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled to room temperature and diluted with excess of cold water. The solid imidazole products that separated out, were filtered, washed with excess of water and was further recrystallized with 9:1 acetone-water to result a pure compound of 1,2,4,5-tetraarylimidazole [9]. **Yield:-** 84% ,M.P: 117°C; IR (cm^{-1},): 3008, 1621, 1521, 1421;

^{1}H NMR ($CDCl_3$/DMSO-*d6*) δ = 7.10–7.91 (m, 20H) ppm; ^{13}C NMR ($CDCl_3$/DMSO-*d*6) δ = 123.2, 124.5, 125.1, 126.0, 127.4, 128.7,128.8, 129.2, 129.5, 129.9, 136.9 ppm.

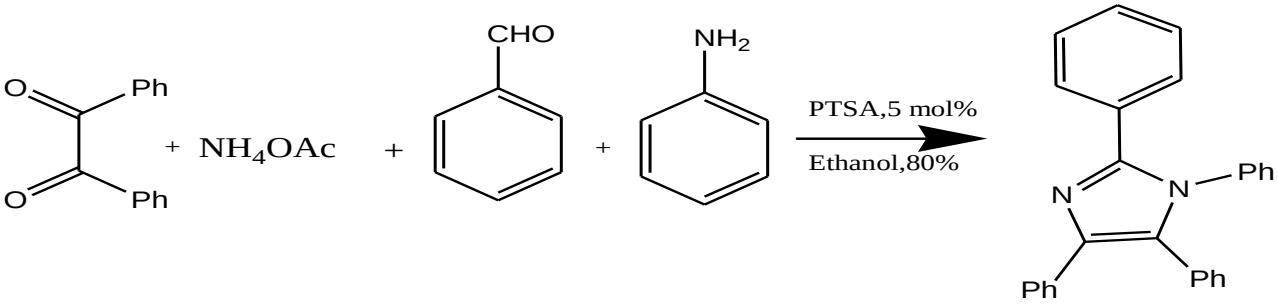

Fig. 2: Synthetic scheme of L2

2.3 Synthesis of Precursor Complexes:

[Ru(bpy)$_2$Cl$_2$].2H$_2$O [P1] :

The mixture of $RuCl_3.H_2O$(250 mg,0.9 mmol),LiCl (405 mg, 9.5mmol), 2,2'-bipyridyl (298 mg, 1.9mmol) were heated at reflux in grade dimethyl formamide (15 mL) for 8 hour. After the reaction mixture was cooled to room temperature, 50 mL of reagent grade acetone was added and the resultant solution cooled at 0^0C overnight. Filtering yielded a red to red-violet solution and a dark-green-black microcrystalline product .The solid was washed three times with 25 mL portions of water followed by three 25 mL portions of diethyl ether, and then it was dried by suction. Finally the black colour product was obtained by filtering it.IR was taken in KBr ,which gives the different values as 3066 cm^{-1} (=C-H); 1672 cm^{-1}(-C=N) ; 1460 cm^{-1}, 1417 cm^{-1} (-C=C-) ; and 3497 cm^{-1}.

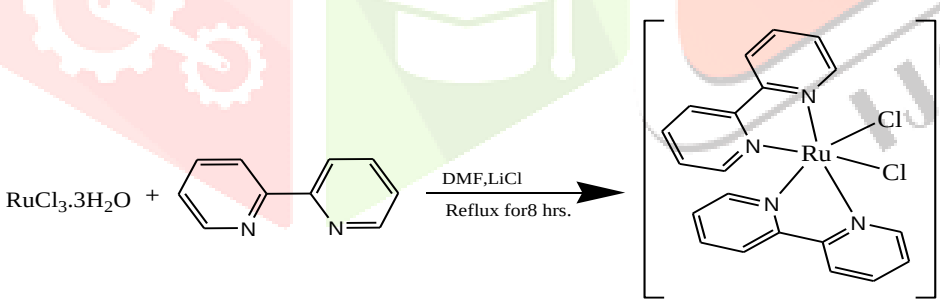

Fig. 3: Synthetic scheme of P1

3. Results and Discussion:

3.1 Synthesis of Cyclometalated complexes:

a) [Ru(bpy)$_2$(2PB-L)]PF$_6$ (1) :

50 mg of [Ru(bpy)$_2$Cl$_2$] precursor and 75 mg of silver nitrate was dissolved in 15 mL of methanol (dried) and heated reflux for 2 hours. The reaction mixture was filtered to avoid the presence of silver chloride. The solution was filtered out .The 2-phenyl-2- benzimidazole was added with 15 mL of DMF to the reaction mixture .The reaction mixture was reflux for 24 hours in nitrogen atmosphere. The dimethyl

formamide was distilled out. Then the reaction mixture is heated on addition of methanol and ammonium hexaphosphate. The mixture is filtered then. The precipitate was washed with hot water and then with ether.

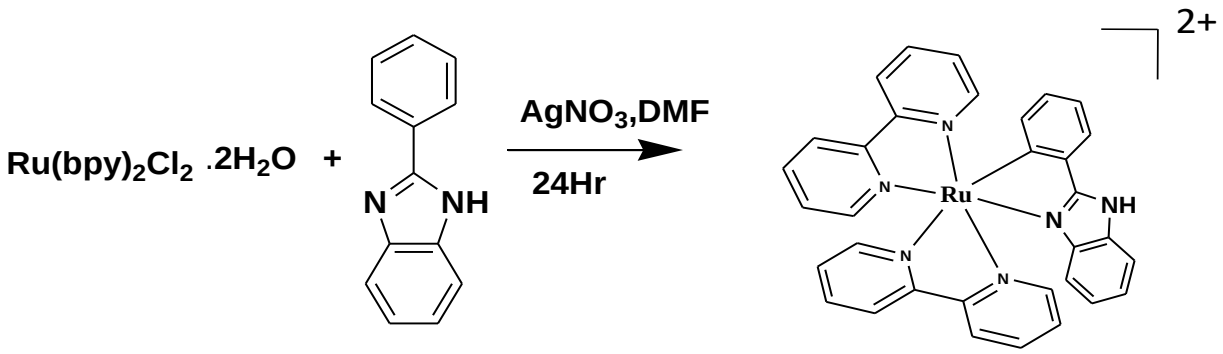

Fig. 4 : Synthetic scheme of complex (**1**)

b) [Ru(bpy)$_2$(1,2,4,5-tetraph-im)]PF$_6$ (2):

[Ru(bpy)$_2$Cl$_2$].2H$_2$O (8mg,0.165mmol);tetra-substituted imidazole (57.26 mg,0.163mmol) was added to the solution of methanol 10mL and dimethoxyethane 10 mL .The solution was reflux by purging nitrogen gas for 1 hours. Then an excess of triethylamine was added and the mixture was refluxed for 24 hours under nitrogen atmosphere. The reaction mixture was concentrated by rotary evaporator and a saturated KPF$_6$ aqueous solution was added to give precipitate. The precipitate was filtered and washed with water and dried. Product was purified by column chromatography using acetonitrile as an eluent.

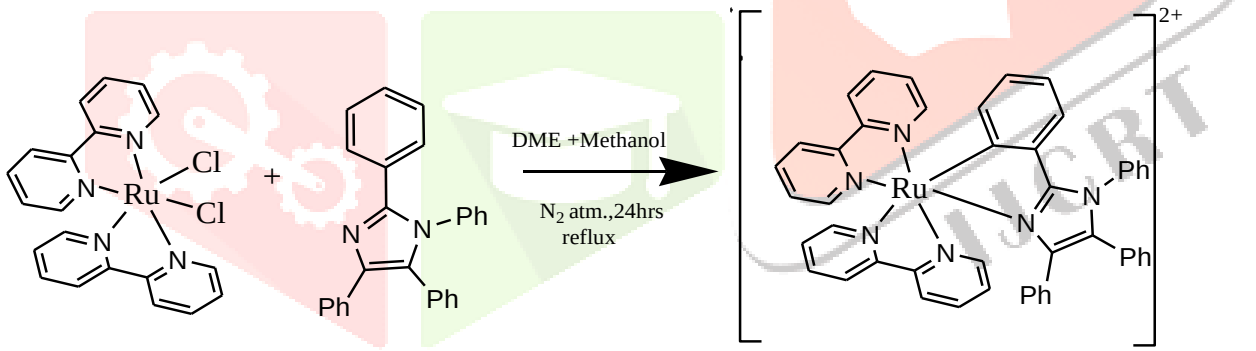

Fig. 5: Synthetic scheme of complex (**2**)

3.2 Characterizations:

3.2.1 UV-VIS Spectroscopy:

The complexes [Ru(bpy)$_2$(2PBL)]PF$_6$, [Ru(bpy)2(1,2,4,5-tetraph-im)]PF6 exhibits the absorption bands at 500-800 nm in visible region due to d-d transition and ligand based π-π^* transition occurs in the UV region of 210-350 nm. The molar extinction coefficient (ε_{max}) value for the complexes were 10^3-10^4 mol^{-1}cm^{-1}in visible region .The corresponding values of each transition in the ligands and metal is shown in spectra along with data-table shown below (Table 1).

3.2.2 IR Spectroscopy:

The solid IR spectrum of the ligand and their complexes has corresponding stretching frequency as given below (Table 2).

Table 1: Photophysical data table: UV-Visible Spectroscopy

COMPLEXES	ABSORBANCE $\lambda_{max}/\varepsilon(M^{-1}cm^{-1})$	
	Acetonitrile	
	Ligand transition	MLCT
[Ru(bpy)$_2$(2PB-L)]PF$_6$	**382**/5000 **295**/39550 **245**/24100	**559**/43000
[Ru(bpy)$_2$(1,2,4,5-tetraph-im)]PF$_6$	**283**/24754.95 **258**/39112.25	**479**/1604.2

Table 2: IR spectral data

Complexes/ligand	-C=C-	-C=N	-C-H	-N-H
1,2,4,5-tetraph-im	1586	1659	2980	3057
[Ru(bpy)$_2$Cl$_2$].2H$_2$O	1460	1616	3066	-
[Ru(bpy)$_2$(1,2,4,5-tetraph-im)]PF$_6$	1587	1663	3057	-

Conclusions:

In the present investigation Cycloruthenated (II) complexes were synthesized and characterized by various spectroscopic analysis. This information is of interest and importance for the design and synthesis of a new cyclometallated ruthenium complexes and utilize it for various application in the field of anticancer activity, catalytic property and photophysical and chemical properties.

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