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Synthesis and Characterization of some CIS $[\text{Ru}(\text{NO})\text{XL}_2(\text{PPh}_3)_2]$ (X=Monodentate) Type Complexes of Nitrosylruthenium (II)

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ABSTRACT

Nitrosyl complexes which have both L= methyl cyanide and triphenylphosphine as coexisting ligands were synthesized and characterised as cis $[\text{Ru}(\text{NO})(\text{X})\text{L}_2(\text{PPh}_3)_2]$; X= OH, Cl, NO₂ and L=CH₃CN. The structures of the complexes have been proposed on the basis of analytical, magnetic and spectroscopic (IR, UV-Visible and ¹H NMR) methods. The properties of these complexes were investigated under the conditions of chemical oxidation and electrochemical reduction.

Key words: Nitrosylruthenium (II), Spectroscopic methods, Chemical oxidation.

INTRODUCTION

The current interest in the metal nitrosyl complexes is mainly due to their novel structure, electrochemical properties and interesting Photoredox chemistry¹⁻⁵. The study of metal nitrosyl under photochemical conditions has attracted much attention due to important role of nitric oxide in biological processes including neurotransmission, tumor growth-inhibition, hepatic metabolism, cell differentiation and blood pressure regulation.⁶⁻¹⁰ Ruthenium nitrosyls $\{\text{Ru NO}\}^6$, however, are more stable and yet exhibit significant degree of photolability of the bound NO. These nitrosyls display their $d\pi(\text{Ru})-\pi^*(\text{NO})$ in uv region (300 – 400 nm). It is, therefore, evident that new approach to sensitise $\{\text{Ru NO}\}^6$ to visible light is required for their successful use¹¹. This biochemical and Physiological properties, completely unforeseen 20yrs ago, is unmistakably responsible for the

renewed interest in the coordination chemistry of transition¹²⁻¹⁶ metal nitrosyls. The reactions of nitric oxide on metals surfaces in contact with metal ions in zeolites is important in the development of catalyst that can reduce atmospheric pollution.¹⁷ The important physiological and environmental role of NO has generated an interest towards the properties and reactions of its metal complexes, especially in case of water soluble ones. For example the reduction of $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ on refluxing in ethanolic KOH and PPh₃, yields $[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$, a catalyst of isomerization of olefins and hydrogenation of olefins, aldehydes and Ketones¹⁸⁻²⁰. It has been found recently that reactivity of metal nitrosyls depends strongly on the nature of coexisting ligands²¹⁻²².

In continuation of our work²³, we report here the synthesis and characterization of $[\text{Ru}(\text{NO})(\text{X})\text{L}_2(\text{PPh}_3)_2]$, X= OH, Cl, NO₂; L=CH₃CN.

EXPERIMENTAL

All the chemicals used were either chemically pure grade or Analar grade. The complexes trans- $[\text{Ru Cl}_2 \text{L}_2(\text{PPh}_3)_2]$ was prepared by the reported method²⁴. All the solvents were dried before use. The elemental analyses (C,H and N) were performed by the Microanalytical laboratory I.I.T Kanpur. Phosphorus and halogens were estimated by standard procedure^{25,26}. IR spectra were recorded with a Perkin Elmer FT IR spectrophotometer in KBr Disc. ¹H NMR spectra were recorded on a varian 300 MHz spectrophotometer in CD_3CN as a solvent and TMS as standard material. Electronic absorption spectra were obtained on cystronic 108 UV-Visible spectrometer from 200-900nm.

Preparation of complexes

$[\text{Ru}(\text{NO})_2 \text{L}_2(\text{PPh}_3)_2] \cdot 2\text{H}_2\text{O}$

To a suspension of Trans $[\text{Ru Cl}_2 \text{L}_2(\text{PPh}_3)_2]$ (100mg) in CH_3CN (30 ml) was added an aqueous solution of NaNO_2 (200mg; 2ml). The mixed solution was refluxed for 1h whereby a homogeneous brown solution formed, was dried by using a rotary evaporator. A small amount of water (5ml) was added to the rotary evaporator, in which some brown crystalline material remained as insoluble matter. The solid material was collected by filtration, washed with water, ethanol, and then ether, and air dried. Yield 75mg. 70%.

$[\text{Ru}(\text{NO})(\text{NO}_2) \text{L}_2(\text{PPh}_3)_2] \cdot (\text{PF}_6)_2$

A suspension of $[\text{Ru}(\text{NO})_2 \text{L}_2(\text{PPh}_3)_2] \cdot 2\text{H}_2\text{O}$ (100 mg) in water (5 ml) was dissolved quickly in hydrochloric acid (0.5 ml) at room temperature to give an orange brown solution. An aqueous solution of NH_4PF_6 (50mg in 5 ml) was added immediately to this orange brown solution whereby a crystalline precipitate of the complex was formed. The product was stored without filtering in a refrigerator for 30 min. It was filtered, washed with cold water, ethanol, and then ether, and air dried. The same compound can also be prepared by adding HPF_6 in place of HCl under the same condition. Yield, 120 mg, 93%.

$[\text{Ru}(\text{NO})(\text{OH})\text{L}_2(\text{PPh}_3)_2] \cdot (\text{PF}_6)_2$

To a suspension of $[\text{Ru}(\text{NO})_2 \text{L}_2(\text{PPh}_3)_2] \cdot 2\text{H}_2\text{O}$ (100 mg) in water (10 ml) were added 2-3 drops trifluoromethanesulphonic acid ($\text{CF}_3\text{SO}_3\text{H}$).

This mixture was refluxed for 5h to give a reddish purple solution. Some powdered NH_4PF_6 (50 mg) was added to the reaction solution. The reddish purple crystalline material which deposited, was collected by filtration, washed with cold water, ethanol, and then ether, and air dried. Yield 115 mg, 92%.

$[\text{Ru}(\text{NO})(\text{Cl}) \text{L}_2(\text{PPh}_3)_2] \cdot (\text{PF}_6)_2$

To a suspension of $[\text{Ru}(\text{NO})_2 \text{L}_2(\text{PPh}_3)_2] \cdot 2\text{H}_2\text{O}$ (100 mg) in water (10 ml) was added some hydrochloric acid (1 ml) and the mixture was refluxed for 2h to give a reddish purple solution. Some powdered NH_4PF_6 (50 mg) was added to the reaction solution. The reddish crystalline material which deposited was collected by filtration, washed with cold water, ethanol and then ether, and air dried. Yield 115 mg, 90% .

$[\text{Ru}(\text{NO}_2)(\text{H}_2\text{O}) \text{L}_2(\text{PPh}_3)_2] \cdot (\text{PF}_6)_2$

To a suspension of $(\text{Ru}(\text{NO})(\text{OH})\text{L}_2(\text{PPh}_3)_2]$ (80 mg) in water (15 ml) was added NaOH solution 1 mol/liter to adjust the pH of the solution to 11.5. The solution was stirred at room temperature overnight, while keeping the pH constant. During this process, the colour of the suspension changes to reddish brown. The product was collected by filtration, washed with ethanol and then ether, and air dried. Yield 60 mg., 86%.

$[\text{Ru}(\text{Cl})(\text{NO}_2)\text{L}_2(\text{PPh}_3)_2] \cdot \text{H}_2\text{O}$

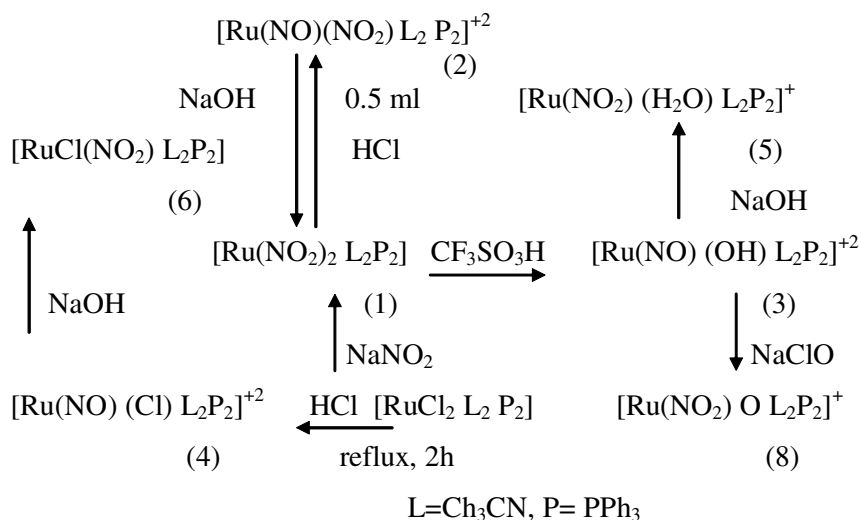
It was prepared by exactly the same procedure as in 5 from $[\text{Ru}(\text{NO})(\text{Cl})\text{L}_2(\text{PPh}_3)_2] \cdot (\text{PF}_6)_2$ and NaOH . Yield 40 mg, 67%.

$[\text{Ru}(\text{NO}_2)_2 \text{L}_2(\text{PPh}_3)_2] \cdot 2\text{H}_2\text{O}$

It was prepared by exactly the same procedure as in 5 from $[\text{Ru}(\text{NO})(\text{NO}_2)\text{L}_2(\text{PPh}_3)_2] \cdot (\text{PF}_6)_2$ and NaOH . Yield 45 mg, 72%.

$[\text{Ru}(\text{NO}_2)_2 \text{O} \text{L}_2(\text{PPh}_3)_2] \cdot \text{PF}_6 \cdot \text{H}_2\text{O}$

To a suspension of $[\text{Ru}(\text{NO})(\text{OH}) \text{L}_2(\text{PPh}_3)_2] \cdot (\text{PF}_6)_2$ (100 mg) in water (5 ml) was added first aqueous solution of NaOH to adjust the pH 10 and then NaClO (1 ml). The mixture was stirred for 2-3 hrs at room temperature; during which period the reddish purple colour of the suspended material became light green. It was collected by filtration, washed with cold water and then dried in vacuo. Yield 60 mg, 67%.



Scheme 1.

All the reactions (1-8) can be Summarised in the following scheme.

RESULTS AND DISCUSSION

Dichloro complexes of Ru⁺² have usually been used as starting materials for the synthesis of the corresponding dinitro complexes of Ru⁺². In the present work trans- [RuCl₂ L₂ (PPh₃)₂] was a useful material. The analytical data of the complexes (Table 1) are in good agreement with the stoichiometry proposed for the complexes. All the complexes were found to be diamagnetic, air stable, soluble in water and insoluble in most of the organic solvents.

IR spectral studies; [Ru(NO) (X) L₂ (PPh₃)₂] (PF₆)₂

- (i) The characteristic²⁷ bands of PPh₃ at 3046, 2671, 1995, 1965, 1466, 1000, 760, 700 and 500 cm⁻¹ were present in the spectra of the complexes.
- (ii) The characteristic bands of CH₃CN was present at 2315 cm⁻¹ in all the complexes.
- (iii) The IR data of ν(NO) are located in the region 1890-1950 cm⁻¹, indicating that nitrosyls complexes are of the {Ru NO}₆ type.²⁸⁻³⁰ Further, in the series of [Ru (NO) (X) L₂ (PPh₃)₂]⁺² complexes, ν(NO) are found to reduce in the order of NO₂>Cl>OH, indicating that the larger π donor ability of the ligand X causes a smaller stretching

frequency of NO.

- (iv) The characteristic³¹ bands of coordinated water molecule were [present at 3400-3500 (broad) due to ν(OH) and 800-760 cm⁻¹ due to δ (OH) in the complexes containing H₂O molecule.

The systematic assignment of the other characteristic bands are given in Table 2.

UV-Visible spectra

The uv-visible spectra of the complexes were recorded from 200-9000 nm. Three intense bands from 280-500 nm were present in all most all the complexes. Their intensities (ε = 10²-10⁴) indicates that these are charge transfer and not d-d transition bands. The bands around 450-500 nm are assigned to dπ (Ru)→P(dπ), 340-360 nm to dπ (Ru)→π*(NO) and around 280-290 nm to intraligand bands. The ligand trans to bound NO has considerable influence on dp(Ru)→π*(NO). An increase in the p donor ability of the ligands OH⁻>Cl⁻>NO₂⁻ brings about red shift of the absorption maximum (λ max). This red shift of C.T. band arises from the increase electron density at the metal center and facilitate dπ(Ru)→π*(NO) transition at the lower energy.³²

¹H nmr spectra

¹H NMR spectra of all the complexes were studied to confirm the presence of coligand

Table 1: Analytical data and colour of the complexes

Compound	Found (%) Calcd							Colour
	Metal	C	H	N	P	Cl	F	
[Ru(NO ₂) ₂ L ₂ (PPh ₃) ₂]2H ₂ O	11.8 (12.1)	56.2 (57.4)	5.1 (4.7)	5.8 (6.7)	7.8 (7.4)	- -		Brown
[Ru(NO)(NO ₂)L ₂ (PPh ₃) ₂](PF ₆) ₂	9.02 (9.4)	45.1 (44.7)	3.6 (3.3)	4.9 (5.2)	11.8 (11.5)	20.8 (21.2)		Orange
[Ru(NO)(OH)L ₂ (PPh ₃) ₂](PF ₆) ₂	9.4 (9.6)	46.3 (45.9)	3.8 (3.5)	3.9 (4.2)	12.2 (11.8)	21.3 (21.8)		Reddish
[Ru(NO)(Cl)L ₂ (PPh ₃) ₂](PF ₆) ₂	9.2 (9.5)	45.3 (45.18)	3.8 (3.5)	3.5 (3.9)	11.9 (11.67)	3.5 (3.3)	21.02 (21.4)	Purple Reddish
[Ru(NO ₂)(H ₂ O)L ₂ (PPh ₃) ₂]PF ₆	10.8 (11.02)	52.8 (52.4)	4.4 (4.1)	4.2 (4.5)	10.4 (10.15)	12.02 (12.4)		Purple Reddish
[RuCl(NO ₂)L ₂ (PPh ₃) ₂]H ₂ O	12.1 (12.5)	59.02 (59.5)	4.9 (4.7)	4.9 (5.2)	6.8 (7.1)	- -		Brown Orange
[Ru(NO ₂)OL ₂ (PPh ₃) ₂] PF ₆ H ₂ O	10.2 (10.8)	51.1 (51.5)	4.2 (4.07)	4.6 (4.5)	10.2 (9.97)	11.8 (12.2)		Brown Green

Table 2: Characteristic IR and uv-visible bands of the complexes

Compound	IR bands					UV-Visible bands λ max (Σ)
	νNO	νCN	ν as(NO ₂) ν s(NO ₂)	ν RuO	ν Ru-cl	
[Ru(NO ₂) ₂ L ₂ (PPh ₃) ₂]2H ₂ O	-	2315	1340 1330	-		455(2.0x10 ²) 326(3.2x10 ²) 288(1.4x10 ³)
[Ru(NO)(NO ₂)L ₂ (PPh ₃) ₂](PF ₆) ₂	1935	2315	1410 1320	-		450(1.0x10 ²) 340(4.1x10 ³) 295(1.4x10 ⁴) 500(9.8x10)
[Ru(NO)(OH)L ₂ (PPh ₃) ₂](PF ₆) ₂	1890	2315				365(5.8x10 ²) 285(8.3x10 ³) 498(1.2x10 ²)
[Ru(NO)(Cl)L ₂ (PPh ₃) ₂](PF ₆) ₂	1920	2318			290	350(4.6x10 ²) 292(5.4x10 ⁴) 460(3.1x10 ²)
[Ru(NO ₂)(H ₂ O)L ₂ (PPh ₃) ₂]PF ₆	-	2318	1330 1274	-		340(1.5x10 ²) 295(2.1x10 ³)
[RuCl(NO ₂)L ₂ (PPh ₃) ₂]H ₂ O	-	2316	1320 1280	-	288	505(2.2x10 ²) 335(4.1x10 ²) 292(8.6x10 ³)
[Ru(NO ₂)OL ₂ (PPh ₃) ₂] PF ₆ H ₂ O	-	2320	1390 1330	806		440(6.5x10 ²) 335(5.2x10 ³) 298(2.8x10 ⁴)

Table 3: Electrochemical data of the [Ru(NO) X L₂(PPh₃)₂]⁺² (X = NO₂, Cl, OH and L = CH₃CN) Complexes

Compound	E (v)				
	E _{pc1}	E _{pa1}	E _{1/2}	ΔE (mv)	E _{pa2}
[Ru(NO)(NO ₂) L ₂ (PPh ₃) ₂] ⁺²	0.25	0.32	0.26	70	-0.80
[Ru(NO)(OH) L ₂ (PPh ₃) ₂] ⁺²	-0.32	-0.24	-0.28	80	-1.12
[Ru(NO)(Cl) L ₂ (PPh ₃) ₂] ⁺²	0.10	0.17	0.13	70	-0.85

E (v) VS Ag /Ag NO₃ (0.1mol/ litre TEAP – CH₃CN at 25°C)

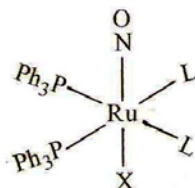
$$E_{1/2} = \frac{(E_{pc1} + E_{pa1})}{2}, \Delta E = |E_{pa1} - E_{pc1}| \text{ mv}$$

molecule. These spectra exhibited a poorly resolved broad multiplets due to 30 protons of phenyl group of PPh₃ at 7.2-7.4 ppm. The additional singlet of 3H of methyl protons of CH₃CN were present at 2.0 ppm.

Based on the IR, uv-visible and ¹H NMR studies of the complexes [Ru(NO)(X) L₂(PPh₃)₂], we propose the following structure.

Electrochemical Reduction

The electrochemical behavior of [Ru(NO)(OH) L₂(PPh₃)₂]⁺² is found similar to other {MNO}⁶ – type complexes with hydroxo ligand.³⁵⁻³⁶ The result of CV experiment (Table 3), shows two one electron reduction. The first wave observed at 0.32 V(E_{1/2}) was reversible, and the second wave was an irreversible wave. The peak potential separation, | E_{pa1} - E_{pc1} | between anodic and cathodic wave is independent of the scan rates. The peak potential



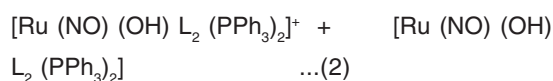
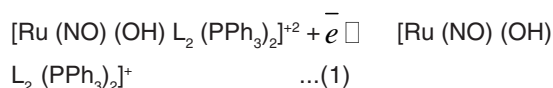
L=CH₃CN

Fig.1

Fig. 1:

Redox Behaviour

Addition of NaClO (dissolved in aqueous basic solution) to [Ru (NO) (OH) L₂ (PPh₃)₂]⁺² gave an Ru⁺⁴ complex which has both nitro and mono oxygen ligands [Ru (NO₂) (O) L₂ (PPh₃)₂]⁺. The oxo ligand formation can be illustrated by the same procedure as that reported else where^{22,33}. Thus, we suggest that nitrosyl and nitro complex are related by the following acid base reaction³⁴.



The site of reduction in the {Ru NO}⁶ complexes is generally confined to the nitrosyl group.

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