



## Synthesis and Characterization of New Ruthenium Nitrosyl Complexes from $[\text{RuCl}_2\text{L}_2(\text{PPh}_3)_2]$ (L = Acetonitril, Acrylonitril, Isobutyronitril, N-benzonitril, Pyridine, Malonitril and Succinonitril)

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### ABSTRACT

Reaction of nitrosothiourea were carried out with  $[\text{RuCl}_2\text{L}_2(\text{PPh}_3)_2]$  (L = acetonitril, acrylonitril, isobutyronitril, n-benzonitril, pyridine, malonitril and succinonitril) in acetone. The product were purified by crystallization and analysed. These complexes have been characterised on the basis of analytical, spectral (IR, UV and Visible) and magnetic studies. The presence of absorption bands at 1625-1635  $\text{cm}^{-1}$  indicates the bent  $\nu\text{M-NO}$  bonding.

**Key words:** New Ruthenium Nitrosyl, IR, UV & Visible studies.

### INTRODUCTION

The research interest in metal nitrosyl chemistry has grown during the recent years with the following four perspectives. (I) to understand the bonding features of NO molecule on metalation as it can bind metal ions as cation  $\text{NO}^+$ , as radical  $\text{NO}^\cdot$ , or as anionic  $\text{NO}^-$ , depending on the electronic nature of ancillary ligands associated with the metal<sup>1,3</sup> ion (II) to explore the condition of photolytic cleavage of M-NO and subsequent transfer of "NO" to biologically relevant target molecule in order to develop alternative molecular devices capable of the functioning as NO donors in biochemical reactions<sup>4,8</sup> ( to understand the electrophilicity of M-NO<sup>+</sup> group by altering the CO ligands (IV) to

understand the mechanism of M-NO./O<sub>2</sub> interaction in biological auto oxidation of free NO<sup>10,12</sup>.

In continuation of our research work<sup>13,14</sup> on metal nitrosyl complexes, we report here the synthesis and characterization of new ruthenium nitrosyl complexes by the reaction of  $[\text{RuCl}_2\text{L}_2(\text{PPh}_3)_2]$  (L = acetonitril, acrylonitril, isobutyronitril, n-benzonitril, pyridine, malonitril and succinonitril) were referred to as ac, ar, isb, ben, py, mal and suc respectively and nitrosothiourea.

### EXPERIMENTAL

All the chemicals used were either chemically pure grade or Analar grade.

$[\text{RuCl}_2\text{L}_2(\text{PPh}_3)_2]$  and nitrosothiourea were prepared by the reported methods<sup>15,16</sup>. All the solvents were dried before use. Phosphorus and halogen were estimated by the standard procedure.<sup>17,18</sup> IR spectra were recorded with a Perkin-Elmer IR spectrometer in KBr disc.

Electronic absorption spectra were obtained on Cystronic 108 UV-Visible spectrometer from 200-900 nm. C,H,N analysis were performed in microanalytical laboratory I.I.T. Kanpur (U.P.), India.

### Preparation of Complexes

#### $[\text{RuCl}_2(\text{NO})(\text{ac})(\text{PPh}_3)_2]$

$[\text{RuCl}_2(\text{ac})_2(\text{PPh}_3)_2]$  (0.75 g, 1 m mol) was taken in 15 ml acetone and added to this a solution of nitrosothiourea 5 ml with constant stirring. The stirring is continued for about 1 hour and the solution is filtered and refluxed for 10 minutes whereby an orange yellow precipitate of the complex was formed. It was filtered and washed several times with acetone, alcohol, ether and dried in vacuo. The complex was crystallized in a acetone + alcohol (1:1) and analyzed.

#### $[\text{RuCl}_2(\text{NO})(\text{ar})(\text{PPh}_3)_2]$

$[\text{RuCl}_2(\text{ar})_2(\text{PPh}_3)_2]$  (0.8 gm, 1 m mole) was dissolved in (20 ml) acetone and nitrosothiourea (5 ml) in water were mixed and stirred at lower temperature (10°C) for 1hr and filtered.  $\text{N}_2$  gas was bubbled in filtrate for 2 hrs resulting a dark brown precipitate of complex. It was filtered, washed several times with acetone, alcohol, ether and dried in vacuo. The complex was crystallized by method 1 and analyzed.

#### $[\text{RuCl}_2\text{NO}(\text{isb})(\text{PPh}_3)_2]$

$[\text{RuCl}_2(\text{isb})_2(\text{PPh}_3)_2]$  (0.9 gm, 1 m mole) in acetone and water solution of nitrosothiourea (5 ml) were mixed and stirred for 2 hrs. and filtered. The solution was cooled in refrigerator for overnight whereby red brown crystals of the complex were separated out. It was filtered and washed several times with acetone, alcohol, ether and dried in vacuo.

#### $[\text{RuCl}_2\text{NO}(\text{ben})(\text{PPh}_3)_2]$

A water solution (5ml) of nitrosothiourea was added drop wise to the stirred solution (20 ml) of  $[\text{RuCl}_2(\text{ben})_2(\text{PPh}_3)_2]$  (0.9 gm in 1m mole) in

acetone at room temperature. The resultant solution was filtered and filtrate was concentrated to 5 ml. On addition of n-hexane, brown crystalline complex separated which was filtered, washed several times with acetone, ether and dried in vacuo.

#### $[\text{RuCl}_2\text{NO}(\text{py})(\text{PPh}_3)_2]$

A water solution of nitrosothiourea (5ml) was added drop wise to a stirring solution of  $[\text{RuCl}_2(\text{py})_2(\text{PPh}_3)_2]$  (0.9g, 1 m mol) in acetone (20 ml) at lower temperature (10°C). After the stirring of 4 hrs, the resultant solution was filtered and filtered was concentrated to 5 ml. On adding ethanol (15 ml), an orange brown crystalline precipitate of the complex separated which was filtered, washed several times with ethanol, ether and dried in vacuo.

#### $[\text{RuCl}_2(\text{NO})(\text{malo})(\text{PPh}_3)_2]$

A suspension of  $[\text{RuCl}_2(\text{malo})_2(\text{PPh}_3)_2]$  (0.9 gm, 1 m mole) in 20 ml methanol and added to this 10 ml of  $\text{CH}_2\text{Cl}_2$  and stirred for 1 hr and filtered. This filtrate was mixed with a water solution of nitrosothiourea (5 ml) at room temperature. This resultant solution was stirred for 1 hr and concentrated to 5 ml. On adding alcohol, a dark red crystal of the complex was formed. It was washed with methanol (5 ml), dichloromethane (5 ml) and dried in vacuo.

#### $[\text{RuCl}_2(\text{NO})(\text{suc})(\text{PPh}_3)_2]$

$\text{RuCl}_2(\text{suc})_2(\text{PPh}_3)_2$  (0.95 gm 1 m mole) was dissolved in acetone-dichloromethane(1:1) by continuous stirring. The resultant solution was filtered and added to this drop wise water solution of (5 ml) nitrosothiourea with constant stirring. The stirring was continuing for about 2 hrs. The resultant solution was filtered and reduced to 5 ml and adding 20 ml methanol, a reddish-brown crystals of the complex separated which was filtered, washed several times with methanol, ether and dried in vacuo.

### Reactions of $[\text{RuCl}_2(\text{NO})\text{L}_2(\text{PPh}_3)_4]$ (L = malonitrile and succenonitrile)

A suspension of 0.9 gm of the complex (1 m mole) was taken in ethanol and  $\text{Cl}_2$  gas was passed under a constant stirring for about 10 minutes. The reaction product was filtered and refluxed on water bath, cooled and petroleum ether (60-80°C) was added whereby orange brown precipitate of the complex was formed. It was filtered

and washed several times with ethanol, ether and dried in vacuo and analyzed.

### RESULT AND DISCUSSION

Literature methods<sup>19,20</sup> for the preparation of hydride, carbonyl and nitrosyl containing triphenylphosphine derivatives of the platinum metals frequently involve multistage reactions or reactions under heterogeneous conditions. Hydrogen, carbon monoxide, nitric oxide and nitrosyl halides are commonly used to provide hydride, carbonyl and nitrosyl ligands in these preparation.

The synthesis of complexes, in this paper, involve a single stage under essentially homogeneous condition and employ nitrosothiourea in place of more hazardous gases as a source of required ligand. The reaction conditions are very simple and permit the achievement of high degree of selectivity and control. We have chosen nitrosothiourea because thiourea is available commercially and nitrosothiourea is easily prepared. Further, it is free from carcinogenic properties<sup>21</sup>.

The change in reaction temperature, solvent, concentration of the ligand or nature of the

**Table 1: analytical data, colour, melting points and magnetic moments of complexes**

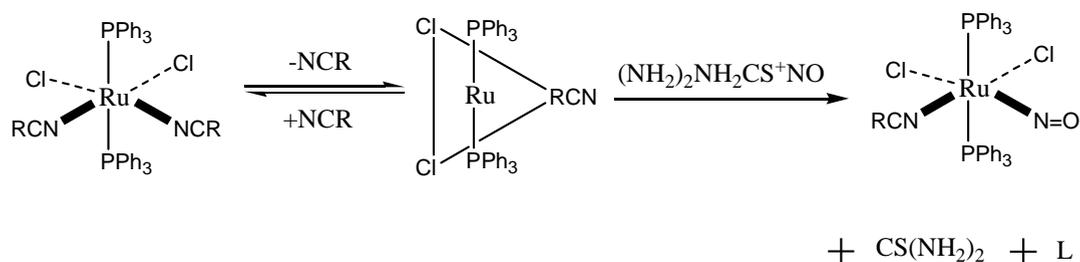
Compounds	Colour	MP °C	Magnetic Moment BM	Found(Calcd)				
				C	H	N	Cl	P
[RuCl <sub>2</sub> (NO)(ac)(PPh <sub>3</sub> ) <sub>2</sub> ]	Orange-yellow	160	1.73	59.05 (59.45)	4.80 (4.30)	3.85 (3.65)	8.8 (8.08)	9.46 (9.26)
[RuCl <sub>2</sub> (NO)(ar)(PPh <sub>3</sub> ) <sub>2</sub> ]	Dark brown	150	1.73	60.27 (60.07)	4.34 (4.24)	3.69 (3.59)	7.90 (7.96)	9.24 (9.14)
[RuCl <sub>2</sub> (NO)(isb)(PPh <sub>3</sub> ) <sub>2</sub> ]	Red brown	165	1.74	60.48 (60.31)	4.96 (4.65)	3.68 (3.52)	7.89 (7.80)	8.90 (8.93)
[RuCl <sub>2</sub> (NO)(ben)(PPh <sub>3</sub> ) <sub>2</sub> ]	Brown	168	1.75	62.43 (62.23)	4.44 (4.22)	3.48 (3.38)	7.60 (7.49)	8.58 (8.56)
[RuCl <sub>2</sub> (NO)(py)(PPh <sub>3</sub> ) <sub>2</sub> ]	Orange-Brown	170	1.74	61.34 (61.11)	4.62 (4.35)	3.56 (3.48)	7.94 (7.70)	8.46 (8.82)
[RuCl <sub>2</sub> (NO)(malo)(PPh <sub>3</sub> ) <sub>2</sub> ]	Dark Red	190	diamagnetic	61.24 (61.33)	4.52 (4.23)	5.20 (5.55)	4.48 (4.70)	8.06 (8.20)
[RuCl <sub>2</sub> (NO)(suc)(PPh <sub>3</sub> ) <sub>2</sub> ]	Reddish brown	195	diamagnetic	62.46 (62.30)	4.62 (4.41)	5.69 (5.45)	4.82 (4.60)	8.20 (8.05)
[RuCl <sub>3</sub> (NO)(suc)(PPh <sub>3</sub> ) <sub>2</sub> ]	Orange	240	diamagnetic	56.50 (56.70)	4.00 (3.90)	2.10 (1.80)	14.20 (13.90)	7.90 (8.10)

**Table 2: Characteristic IR bands of ligands and complexes**

Compounds	vCN	vNO	vRu-Cl
[RuCl <sub>2</sub> (NO)((ac)(PPh <sub>3</sub> ) <sub>2</sub> ]	2315, 2288	1625	275, 268
[RuCl <sub>2</sub> (NO)(ar)(PPh <sub>3</sub> ) <sub>2</sub> ]	2237, 2230 vC=C at 1600	1628	277, 270
[RuCl <sub>2</sub> (NO)(isb)(PPh <sub>3</sub> ) <sub>2</sub> ]	2262, 2252	1630	300, 284
[RuCl <sub>2</sub> (NO)(ben)(PPh <sub>3</sub> ) <sub>2</sub> ]	2243, 2228	1628	299, 285
[RuCl <sub>2</sub> (NO)(py)(PPh <sub>3</sub> ) <sub>2</sub> ]	-	1635	294, 275
[RuCl <sub>2</sub> (NO)(malo)(PPh <sub>3</sub> ) <sub>2</sub> ]	2212 broad	1630	310 broad
[RuCl <sub>2</sub> (NO)(suc)(PPh <sub>3</sub> ) <sub>2</sub> ]	2262, 2231	1628	275, 256
[RuCl <sub>3</sub> (NO)(suc)(PPh <sub>3</sub> ) <sub>2</sub> ]	-	1880	275, 268

reagents provide a route to the range of pure complexes. Further, the solubilities of these of the complexes in alcoholic solvents used in these reactions ensure the rapid precipitations or

crystallizations of required product in a good yield. Treatment of  $[\text{RuCl}_2\text{L}_2(\text{PPh}_3)_2]$  with one equivalent of nitrosothiourea in acetone, afforded compounds  $[\text{RuCl}_2(\text{NO})\text{L}(\text{PPh}_3)_2]$ . The reaction is believed to occur by the following way.



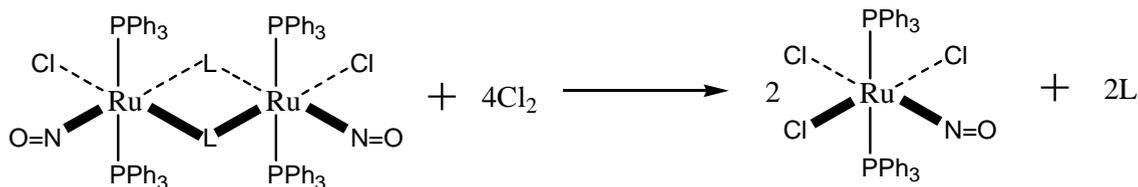
The analytical data (Table 1) are in good agreement with the stoichiometry proposed for the compound. The nitrosyl compound with (L=ac, ar, isb, ben, py) were found to be paramagnetic and non ionic in nature. The nitrosyl compounds with L= malonitrile and succinonitrile are found to be diamagnetic in nature. The compounds are in general air stable and

soluble in most of the organic solvent such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CH}_3\text{CHO}$ , DMF, DMSO,  $\text{CH}_3\text{CN}$  and pyridine. Further, the nitrosyl complexes with L = malonitrile and succinonitrile undergo reactions with  $\text{Cl}_2$  gas to produce  $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ .<sup>22</sup> Based on this reaction, we initially propose the following structures of the complexes.

**Table 3: Assignments of uv and visible bands of complexes**

Compounds	Position or the absorption bands ( $\text{cm}^{-1}$ )		Assignments
$[\text{RuCl}_2(\text{NO})(\text{ac})(\text{PPh}_3)_2]$	19200	520	a
	20400	490	b
	31800	314	CT
$[\text{RuCl}_2(\text{NO})(\text{ar})(\text{PPh}_3)_2]$	19100	523	a
	20200	495	b
	31500	317	CT
$[\text{RuCl}_2(\text{NO})(\text{isb})(\text{PPh}_3)_2]$	19150	522	a
	20200	495	b
	31500	317	CT
$[\text{RuCl}_2(\text{NO})(\text{ben})(\text{PPh}_3)_2]$	20000	500	a
	21200	465	b
	32000	312	CT
$[\text{RuCl}_2(\text{NO})(\text{py})(\text{PPh}_3)_2]$	20000	500	a
	21200	465	b
	32000	312	CT
$[\text{RuCl}_2(\text{NO})(\text{malo})(\text{PPh}_3)_2]$	19000	526	c
	31800	314	CT
$[\text{RuCl}_2(\text{NO})(\text{suc})(\text{PPh}_3)_2]$	18850	530	c
	31500	317	CT

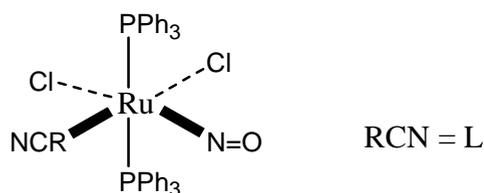
a =  ${}^2\text{T}_{2g} \rightarrow {}^2\text{T}_{1g}$ , b =  ${}^2\text{T}_{2g} \rightarrow {}^2\text{A}_{1g}$ , c =  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$  or  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$  CT = Charge Transfer



**IR Spectra of  $[\text{RuCl}_2\text{NOL}(\text{PPh}_3)_2]$  (L = acetonitrile, acrylonitrile, isobutyronitrile, n-butyronitrile, benzonitrile and pyridine)**

- (A) The characteristic bands<sup>15</sup> of acetonitrile, acrylonitrile, isobutyronitrile, n-butyronitrile, benzonitrile and pyridine were present in their respective complexes (Table 2).
- (B) The characteristic bands of triphenyl phosphine<sup>23</sup> at 3050, 2670, 1975, 1965, 1885, 1820, 1760, 1660, 1570, 1470, 1460, 1320, 1300, 1180, 1090, 1000, 760, 700 and  $500\text{ cm}^{-1} (\pm 5\text{ cm}^{-1})$  were present in all the complexes.
- (C) The bands of weak intensity at  $325\text{-}340\text{ cm}^{-1}$  in the IR spectra of these complexes were present, these bands are assigned to  $\nu\text{Ru-Cl}$ .
- (D) The absorption bands at  $1625\text{-}1635\text{ cm}^{-1}$  in all the complexes is assigned to bent  $\delta\text{M-NO}$ .

The systematic assignments of all these bands are given in Table 2. Thus, IR spectral studies indicates the following bonding scheme for complexes.



**Fig. 1:**

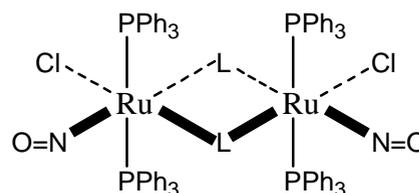
**IR Spectra of  $[\text{Ru}_2\text{Cl}_2(\text{NO})_2\text{L}_2(\text{PPh}_3)_4]$  (L = malonitrile and succinonitrile)**

- (A) The characteristic bands of malonitrile and succinonitrile were present<sup>15</sup> in the IR spectra of the complexes. (Table 2.2)
- (B) The characteristic bands of triphenylphosphine<sup>23</sup> at 3046, 2671, 1975,

1965, 1885, 1820, 1760, 1666, 1572, 1472, 1466, 1320, 1300, 1180, 1090, 1000, 760, 700 and  $500\text{ cm}^{-1} (\pm 5\text{ cm}^{-1})$ .

- (C) The bands of weak intensity at  $325\text{-}340\text{ cm}^{-1}$  in the IR spectra of these complexes are assigned to  $\nu(\text{Ru-Cl})$ .
- (D) The absorption bands at  $1625\text{-}1635\text{ cm}^{-1}$  in these complexes is assigned to bent  $\nu\text{M-NO}$ .
- (E) IR spectral studies of  $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)]$  show the characteristic frequencies of  $\text{PPh}_3$  and  $\text{Ru-Cl}$  bond. Besides these, a very strong band at  $1880\text{ cm}^{-1}$ , indicates the presence of nitrosyl ligand as  $\text{NO}^+$ .

Thus on the basis of IR spectral studies, reactivity of with  $\text{Cl}_2$  and magnetic properties of the complexes  $[\text{Ru}_2\text{Cl}_2(\text{NO})_2\text{L}_2(\text{PPh}_3)_4]$ , the following tentative structure is proposed.



**Fig. 2:**

**Magnetic Properties**

The paramagnetic behavior of  $[\text{RuCl}_2(\text{NO})\text{L}(\text{PPh}_3)_2]$   $\mu_{\text{eff}}$  (1.73- 1.75 BM) indicates the presence of one unpaired electron, suggesting the ruthenium in +1 or +3 state. The nitrosyl ligand can act as one electron donor bent  $\nu\text{M-NO}$  at  $1525\text{-}1690\text{ cm}^{-1}$  or three electron donor linear  $\nu\text{M-NO}$  at  $1800\text{-}1900\text{ cm}^{-1}$ . The lower frequency of NO ligand in all these complexes suggests the presence of +3 states. The charge balance along with magnetic data further supports the proposed structure (Fig 2).

The diamagnetic behavior of the complexes  $[\text{Ru}_2\text{Cl}_2(\text{NO})_2\text{L}_2(\text{PPh}_3)_4]$  (L= malonitrile

and succinonitrile), indicates the spin pairing, suggesting the presence of ruthenium +2 state. The absorption bands of nitrosyl ligand in these complexes were found at 1625-1630  $\text{cm}^{-1}$ . The diamagnetic behavior, charge balance and chemical reactivity of complexes with  $\text{Cl}_2$  gas, further supports the proposed structure of complexes (Fig 2).

### Electronic Spectra

The electronic spectra of the complexes  $[\text{RuCl}_2(\text{NO})\text{L}(\text{PPh}_3)_2]$  (L= aceto nitrile, acrylonitrile, isobutyronitrile, n-butyronitrile, benzonitrile and pyridine) and  $[\text{RuCl}_2(\text{NO})\text{L}_2(\text{PPh}_3)_4]$  (L= malonitrile and succinonitrile) were recorded in  $\text{CH}_2\text{Cl}_2$  from 300-800 nm. The position of absorption bands ( $\text{cm}^{-1}$ ) their assignments are given in Table 3.

Ru(+3) system in octahedral environment is expected to exhibit<sup>26,28</sup> three spin allowed bands from 18000-22000  $\text{cm}^{-1}$ . These bands are due to

${}^2\text{T}_{2g} \rightarrow {}^2\text{T}_{1g}$ ;  ${}^2\text{T}_{2g} \rightarrow {}^2\text{A}_{2g}$  and  ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ . However, only two bands of very low intensity ( $\lambda \sim 15$ ) appear and third band is masked probably by very intense charge transfer bands. This charge transfer band which is assigned to M'L charge transfer. The appearance of these bands along with magnetic properties suggest the octahedral environment of the ligands around Ru(+3).

Ru(+2), a  $d^6$  system environment of ligands is expected to exhibit four bands  ${}^1\text{A}_{1g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^1\text{T}_{1g}$  and  ${}^1\text{T}_{2g}$  transitions. The spectra of these complexes show bands around 19000  $\text{cm}^{-1}$  and 32000  $\text{cm}^{-1}$ . Most of the weak d-d bands were therefore masked by charge transfer bands around 32000  $\text{cm}^{-1}$ . The bands around 19000  $\text{cm}^{-1}$  are assigned to either  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$  or  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$  analogous to other Ru(+2) complexes.<sup>29,30</sup> The presence of these bands indicates the octahedral environment of the ligand around Ru(+2) in  $[\text{RuCl}_2(\text{NO})\text{L}(\text{PPh}_3)_2]$  (L= malonitrile and succinonitrile).

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