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# Synthesis and Characterization of New Rhodium Nitrosyl Complexes with General Formula [RhX<sub>2</sub> (NO) L<sub>2</sub>] (X = Cl, Br, PPh<sub>3</sub>, PEtPh<sub>2</sub> and PEt<sub>2</sub>Ph)

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## ABSTRACT

The reaction of nitrosothiourea were carried out with  $[RhHX_2L_2]$  (X = CI, Br; L = PPh<sub>3</sub>, PEtPh<sub>2</sub> and PEt<sub>2</sub>Ph) in alcohol. The product were purified, analysed and characterized on the basis of analytical, spectral (IR, UV and Visible) and magnetic studies. A tentative structure to all the complexes have been proposed.

Key words: New Rhodium Nitrosyl complex, IR, UV and Visible studies.

#### INTRODUCTION

Nitrosyl ligand has been shown to exist as radical NO<sup>-</sup>, as cation NO<sup>+</sup> or as anionic NO<sup>-</sup>, depending on electronic structure of metal and coordinating abilities of co-ligands.<sup>1</sup> Crystallographic and spectroscopic studies have been used to distinguish between the mode of linkage of nirtosyl ligand.<sup>2-5</sup> The role of NO in biological processes such as neuro-segaling,<sup>6</sup> cardiovascular control<sup>7</sup> or defence mechanisms against microorganism and tumor cells<sup>8</sup> prompted an intense renewed research interest towards nitrosyl coordination chemistry. During the recent years the research interest has grown extensively on the metal nitrosyl species (L){M-NO} with the main complexes on the following aspects (a) designing of (L){M-NO} species that are capable of delivering free NO to biological targets under mild photolytic condition<sup>9</sup> (b) the stabilization of one or more redox states of nitric oxide<sup>10</sup> (c) mechanistic aspects of interaction between suitable nucleophilic/electriphilic on M-NO center.<sup>11</sup>

In continuation of our research interest in nitrosyl transition metal complexes,<sup>12,13</sup> we report here in the synthesis and characterization of [RhX<sub>2</sub> (NO) L<sub>2</sub>] (X = Cl, Br, L = triphenyl phosphine (PPh<sub>3</sub>), ethyldiphenyl phosphine (PEtPh<sub>2</sub>) and diethylphenyl phosphine (PEt<sub>2</sub>Ph)) obtained by the reaction of RhHX<sub>2</sub>L<sub>3</sub>] and nitrothiourea.

## EXPERIMENTAL

All the chemicals used were either chemically pure grade or Analar grade. [RhHX<sub>2</sub>L<sub>3</sub>] and nitrosothiourea were prepared by the reported procedure.<sup>14,15</sup> All the solvents were purified before use. Metal phosphorus and halogens were estimated by the standard procedure.<sup>16,17</sup>IR spectra were recorded with a Perkin-Elmer IR spectrometer in KBr disc. Electronic absorption were obtained on Cystronic 108 UV-Visible spectrometer from 200-900 nm. C,H and N analysis were performed in microanalytical laboratory I.I.T. Kanpur (U.P.), India.

# Preparation of nitrosyl rhodium Complexes Dichloro(nitrosyl)bis(triphenylphosphine)rhodium (III) [RhCl<sub>2</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>]

To a warm alcoholic (20 ml) solution of  $[RhHCl_2(PPh_3)_3]$  (1 gm,1 mmole) was added 10 ml solution of (1: 1 v/v, alcohol : water) nitrosothiourea with a constant stirring. After a stirring of 2 hrs. and subsequent, the complex was separated as brown needles. It was filtred, washed successively with ethanol, ether, and dried in vacuo.

# Dichloro(nitrosyl)bis(ethyldiphenylphosphine)rhodium (III) [Rh Cl<sub>2</sub>(NO)(PEt Ph<sub>2</sub>)<sub>2</sub>]

To a warm alcoholic solution (20 ml) of  $[RhHCl_2(PEtPh_2)_3]$  (0.80 gm,1 mmole) was added 10 ml (1 : 1 v/v ethenol : water). solution of nitrosothiourea with constant stirring for about 10 minutes. The stirring was continued for about 1.5 hrs. and then the reaction mixture was refluxed for 10 minutes followed by cooling in refrigerator, a light brown prisms of the complex was formed. It was filtered and washed successively by water and methanol and dried and vacuo.

## Dichloro(nitrosyl)bis(diethylphenylphosphine)rhodium (III) [Rh Cl<sub>2</sub>(NO) (PEt Ph),]

A warm solution (20 ml) of  $[RhHCl_2 (PEt_2 Ph_)_3]$  (0.70 gm,1 mmole) in alcohol was mixed rapidly with a freshly prepared solution (10 ml) of nitrosothiourea (1 : 1 v/v water : ethanol). The solution was stirred for about 1 hour and refluxed for about 2 hours. It was concentrated to 1 ml and cooled whereby dark brown needles of the complex was formed, filtered and washed successively with water, methanol and dried in vacuo.

# Dibromo(nitrosyl)bis(triphenylphosphine)rhodium (III) [RhBr<sub>2</sub>(NO) (PPh<sub>3</sub>)<sub>2</sub>]

A warm solution (20 ml) of  $[RhHBr_2(PPh_3)_3]$  (1.1 gm,1 mmole) in alcohol was mixed immediately with the freshly prepared solution (10 ml) of nitrosothiourea (1 : 1 v/v water : ethanol). The reaction mixture was stirred for 2 hrs. then refluxed for 20 minutes. It was concentrated to 10 ml and cooled whereby brown precipitate of the complex formed, was filtered and washed several times with water, methanol and dried and vacuo. It was recrystallized from dichloromethane – methanol solution whereby brown needles of the complex appeared.

# Dibromo(nitrosyl)bis(ethyldiphenylphosphine)rhodium (III) [Rh Br, NO (PEt Ph,),]

A warm solution (20 ml) of  $[RhBr_2 (PEtPh_2)_3]$  (0.90 gm,1 mmole) in alcohol was mixed immediately with the freshly prepared solution of nitrosothiourea (10 ml, 1 : 1 v/v water : ethanol). The mixture was stirred for 2 hrs. and heated under refluxed for 10 minutes. The reaction mixture was cooled whereby a maroon coloured complex was formed, was filtered, washed several times with water, methanol and recrystallized as maroon needles from diechloromethane – methanol.

## Dibromo(nitrosyl)bis(diethylphenylphosphine)rhodium (III) [Rh Br, (NO) (PEt, Ph),]

To a continuously stirred ethanolic solution (20 ml) of  $[RhHBr_2 (PEt_2Ph)_3]$  (0.75 gm, 1 mmole) was added freshly prepared solution (10ml) of nitrosothiourea (1 : 1 v/v water : ethanol). The reaction mixture was heated under refluxed for about 1 hour. It was cooled whereby red brown precipitate of the complex formed. It was filtered and washed several times with water, methanol and dried in vacuo. It was recrystallized as red brown platelets from diechloromethane – methanol

#### **RESULTS AND DISCUSSION**

Rhodium and Irridium halogenonitrosyl complexes,  $MX_2NO(APPh_3)_2$  (X= CI, Br or I, A = P or As) are well known.<sup>18,19</sup> The chloro derivatives have been synthesized by variety of ways including reaction of preformed chloride complexes<sup>20</sup> or metal chlorides and nitric oxide with triphenylphosphine or arsine in organic solvents. The method we have

employed is more convenient than the previous one. Since it involves only a single rapid reaction and avoids the use of gaseous nitric oxide or nitrosyl halides. Further more, the basic technique appears to be readily capable of application to the synthesis of halogenonitrosyl complaxes containing a wide variety of phosphine, arsine or stilbine ligands.

In each synthesis a solution of appropriate complex  $[RhHX_2L_3]$  (X = Cl, Br, L = PPh<sub>3</sub>, PEtPh<sub>2</sub>and PEt<sub>2</sub>Ph) in boiling solvent in treated rapidly with (1 : 1 v/v water : ethanol) a solution of freshly prepared nitrosotheourea. The reaction mixture is stirred for some time and heated under reflux (usually 10-20 min) until the precipitation of the product occurs or until the reaction is complete. The cooled solution is then concentrated under vacuum. In several cases involving ethyldiphenylphospine or diethylphenylphosphine, the crystalization is added by the presence of a small volume of water in the reaction mixture.

The analytical data (Table 1) and charge balance are in good agreement with the stoichiometry proposed for the complexes. The physical properties of  $[RhX_2(NO)L_2]$  (X = Cl, Br, L = PPh<sub>3</sub>, PEtPh<sub>2</sub> and PEt<sub>2</sub>Ph), show expected dependence on the nature of the phosphine ligands present in the molecule. Complexes with triphenylphosphine are insoluble in all common organic solvents and melt at 160-260°C usually with extensive decomposition. These complexes with ethyldiphenylphosphine or diethylphenylphosphine are more soluble in organic solvents and frequently melt at lower temperatures with decomposition.

Table	1: Analy	vtical	data.	colour.	meltina	points an	d magnetic	moments	of com	nplexes
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Compounds	Colour	MP	Magnetic	Found(Calcd) %					
		٥C	Moment	С	Н	Ν	Р	CI	Rh
[RhCl <sub>2</sub> (NO)(PPh <sub>3</sub> ) <sub>2</sub> ]	Brown	210	D	58.86	4.46	1.82	9.10	10.74	13.86
				(59.01)	(4.09)	(1.91)	(8.74)	(10.24)	(14.07)
[RhCl <sub>2</sub> (NO)(PEtPh <sub>2</sub> ) <sub>2</sub> ]	Light	145	D	52.46	5.10	1.98	10.34	11.92	15.78
	brown			(52.80)	(4.71)	(2.20)	(10.06)	(11.79)	(16.19)
[RhCl <sub>2</sub> (NO)(PEt <sub>2</sub> Ph) <sub>2</sub> ]	Dark	138	D	44.82	5.64	2.20	12.08	14.02	18.94
2 2.2	brown			(44.44)	(5.55)	(2.59)	(11.85)	(13.88)	(19.07)
[RhBr <sub>2</sub> (NO)(PPh <sub>2</sub> ) <sub>2</sub> ]	Orange	230	D	52.56	4.02	1.58	7.42	19.84	11.96
- 2 3 2-	brown			(52.87)	(3.67)	(1.71)	(7.83)	(19.58)	(12.60)
RhBr <sub>2</sub> (NO)(PEtPh) <sub>2</sub>	Red	170	D	46.24	4.62	1.74	8.34	21.92	14.02
2	brown			(46.60)	(4.16)	(1.94)	(8.87)	(22.19)	(14.28)
RhBr <sub>a</sub> (NO)(PEt <sub>a</sub> Ph) <sub>a</sub>	Dirty	160	D	37.94	5.10	1.96	10.54	25.98	16.86
2 2 2 2	brown			(38.40)	(4.80)	(2.24)	(10.24)	(25.60)	(16.48)

Table 2: Assignments of mejor IR bands of the ligand in complexes

Compounds	vNO cm <sup>-1</sup>	vM-Cl cm <sup>-1</sup> vM-Br
RhCl <sub>2</sub> (NO)(PPh <sub>3</sub> ) <sub>2</sub>	1630	340s
$RhCl_{2}(NO)(PEtPh_{2})_{2}$ $RhCl_{2}(NO)(PEt_{2}Ph)_{2}$	1630 1628	340 340
$RhBr_{2}(NO)(PPh_{3})_{2}$ $RhBr_{2}(NO)(PEtPh_{2})_{2}$	1634 1634	269m 270
RhBr <sub>2</sub> (NO)(PEt <sub>2</sub> Ph) <sub>2</sub>	1632	270

#### Mechanism of the formation

The reactions of mnts (N-methyl–N– nitrosotoluene–p–sulph onamide) with metal hydride complexes to yield nitrosyl derivatives are well known.<sup>21-23</sup> The formation of nitrosyl complexes in these reactions occur by attack in situ on hydride complexes. In our reaction of nitrosothiourea with rhodium hydride complexes, we believe that nitrosyl derivatives of rhodium complexes is formed similarly by attack in situ on hydride complexes.

The nitrosothiourea is formed by the following reactions.:

$$H^+$$
 + HNO<sub>2</sub> + CS(NH<sub>2</sub>)<sub>2</sub>  $\xrightarrow{k}_{\text{first}}$  (NH<sub>2</sub>)<sub>2</sub> CS<sup>+</sup> NO  $\xrightarrow{k_1}_{\text{first}}$ 

 $H^{+} + (NH_{2}) (N-H) CS + NO \xrightarrow{h_{2}} NH_{2}CSNHNO$ 

The nitrosothiourea formed as a result of the above reaction is allowed to react with  $[RhHX_2L_3]$  as :

$$[RhHX_1L_1] + NH_1CS NHNO \longrightarrow [RhX_1(NO)L_1] + L + (NH_1)_1CS$$

The structural studies of the complexes were carried out on the brain of spectral and magnetic measurements as follows :

#### **IR Spectra**

1 The value of v(NO) recorded for the complexes appear in the range of 1630-1635 cm<sup>-1</sup> and show marked dependence on the nature of the phosphine ligands. It is almost independent on the nature of X= CI or Br. v(NO) is slightly higher for L= PEtPh<sub>2</sub> or PEt<sub>2</sub>Ph, indicating a poor  $\pi$ -bonding nature of these ligands than triphenylphosphine. Further, the position of nitrosyl band n(NO) in IR spectra of the rhodium nitrosyl derivatives [RhX<sub>2</sub>(NO)L<sub>3</sub>] is not appreciably affected (<10 cm<sup>-1</sup>) by change of medium from Nujol mull to dichloromethane solution and we therefore conclude the essentially the same molecular structure prevails for the complexes in solid state and in solution. However, the splitting of nitrosyl band observed in some of the solid state spectra (Nujol mull), are tentatively attributed to solid state effects. This is absent in corresponding solution spectra.

- 2. The characteristic absorption bands of PPh<sub>3</sub><sup>24</sup> at 3050, 2675, 1975, 1965, 1885, 1820, 1760, 1665, 1585, 1435, 1320, 1300, 1180, 1155, 1090, 760, 700 and 500cm<sup>-1</sup> (±5cm<sup>-1</sup>) were found in triphenylphosphine complexes. The characteristic bands of PEtPh<sub>2</sub> or PEt<sub>2</sub>Ph<sup>25</sup> were found at 3060, 2950, 2860, 2675, 1970, 1960, 1880, 1825, 1765, 1670, 1580, 1440, 1320, 1310, 1200, 1160, 1100, 760, 700 and 500 cm<sup>1</sup> (± 5 cm<sup>-1</sup>) were found in [RhX<sub>2</sub>(NO)L<sub>2</sub>] (X= CI, Br , L = PEtPh<sub>2</sub>, PEt<sub>2</sub>Ph).
- 3. The absorption  $bands^{26}$  in the region 324-340cm<sup>-1</sup> in the spectra of  $[RhCl_2(NO)L_2]$  (L = PPh<sub>3</sub>, PEtPh<sub>2</sub>, PEt<sub>2</sub>Ph) are assigned to metal chorine stretching vibrations. The absorption bands in the region 215-270 cm<sup>-1</sup> in the spectra of  $[RhBr_2(NO)L_2]$  (L = PPh<sub>3</sub>, PEtPh<sub>2</sub>, PEt<sub>2</sub>Ph) are assigned to metal-bromine stretching vibrations.

These bands are justified because vRh-Cl should appear at an higher frequency than vRh-Br. These bands in the region are associated with terminal metal-chlorine or metal-bromine vibrations.<sup>27</sup>

The X-ray crystallography of some of the complexes  $[MX_2(NO)L_2]$  (X = CI, Br, I, M= Rh, Ir and L= PPh<sub>3</sub>, AsPh<sub>3</sub>) have been performed.<sup>28</sup> By comparing the IR spectral pattern of these complexes with  $[RhX_2(NO)L_2]$ , we conclude that possibly nitrosyl group is bonded in a non linear manner. Thus, the structure is best described as distorted square pyramidal. The nitrosyl ligand occupying the optical site with trans phosphine and trans chlorine in the basal plane.



Fig. 1:

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#### **Magnetic Studies**

All the complexes  $(RhX_2(NO)L_2)$  are diamagnetic, indicating the presence of Rh as +1 or +3. Nitrosyl ligand can act as one electron donor (bent NO, nNO at 1525-1690 cm<sup>-1</sup>) or three electron donor linear NO, nNO at (1800-1900 cm<sup>-1</sup>).<sup>29</sup> The lower frequency of NO ligand in all these complexes suggest the presence of nitrosyl ligand as NO<sup>-</sup>. Thus, the charge balances in these complexes, suggest the presence of Rh in +3 state.

# **Electronic Spectra**

The electronic spectral studies of all the complexes were carried out in order to know the arrangement of ligands around metal ion. The spectra were scanned in  $CH_2CI_2$  from 200-900 nm. Only very intense bands at 340 and 350 nm were observed in all the complexes. The very high intensity of these bands suggest that they should be charge transfer and not d-d transition bands.

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