



## Reaction of N-ethoxycarbonylpyrrole-2-thiocarboxamide and N-phenylcarbamoylpyrrole-2-thiocarboxamide with $[\text{Rh NOX}_2 (\text{PPh}_3)_2]$ ( $\text{X}=\text{Cl}^-, \text{Br}^-, \text{I}^-$ and $\text{NO}_2^-$ )

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### ABSTRACT

In this paper, the reaction of  $[\text{RhX}_2\text{NO}(\text{PPh}_3)_2]$  ( $\text{X}=\text{Cl}^-, \text{Br}^-, \text{I}^-$  and  $\text{NO}_2^-$ ) were Carried out with N-ethoxycarbonylpyrrole-2-thiocarboxamide (ETH) and N-phenylcarbamoylpyrrole-2-thiocarboxamide (PTH). The product were analyzed and Characterized by spectral (IR,UV and Visible) and magnetic moment studies.

**Key words:** Reactions, Thiocarboxamide derivative.

### INTRODUCTION

Nitric Oxide is a versatile ligand for Coordination and Organometallic compounds. It can bind transition metals as a linear or bent molecule ( $\text{NO}^\ominus$ ). The over all structure and reactivity features of metal nitrosyls has been classically rationalized in terms of their  $[\text{MNO}]^n$  description. Where n stands for total number of metal d electrons and nitrosyl  $\delta^+$  electrons. This description was given by Enemark and Fetham<sup>1</sup>. Thousands of metal nitrosyls are known out of which 2200 compounds having linear M-NO ( $\text{NO}^+$ ) have been fully characterised. It has been Observed that lability of M-NO bond depends on Coligands donor atoms, electron delocalization inside the ligands, solvent and steric effects.<sup>2</sup>

### EXPERIMENTAL

N-Ethoxycarbonylpyrrole-2-thiocarboxamid and N-Phenylcarbamoylpyrrole-2-thiocarboxamide were prepared according +to the procedure described in  $[\text{RhX}_2\text{NO}(\text{PPh}_3)_2]$  ( $\text{X}=\text{Cl}^-, \text{Br}^-, \text{I}^-$  and  $\text{NO}_2^-$ ) were prepared according to the method described else where.<sup>3,4</sup>

#### Preparation of Metal Complexes

##### $[\text{Rh NO}(\text{Cl})_2 (\text{ETH})_2]$

To a suspension of  $[\text{RhCl}_2\text{NO}(\text{PPh}_3)_2]$  (0.18g, 0.25mmol) in THF (10ml) was added 2 equivalent of ETH (0.1g, 0.50mmol), and the reaction mixture was stirred at room temperature for 5h. The solvent was removed and the residue was extracted with hexane-  $\text{Et}_2\text{O}$ (1:1V1V ). Concentration and cooling at  $-10^\circ\text{C}$  afforded deep red crystals.

**[Rh NO(Br<sub>2</sub>) (ETH)<sub>2</sub>]**

A mixture of [Rh Br<sub>2</sub> NO(PPh<sub>3</sub>)<sub>2</sub>] (0.20g, 0.25mmol) and two equivalent of ETH (0.1g, 0.50mmol) in THF (10ml) was heated at reflux for 1h. The solvent was pumped off and the residue was washed with hexane. Recrystallization from Et<sub>2</sub>O-hexane (1:1V1V) afforded dark brown crystals.

**[Rh NO(I<sub>2</sub>) (ETH)<sub>2</sub>]**

An excess of lithium iodide (0.15g) was added to a solution of dichoronitrosyl rhodium (I) (0.05g) in acetone (5ml) and the mixture was shaken for Ca. 1min. 0.28g of ETH was added to this solution and the mixture was heated under reflux for 1h. The violet brown crystals which separated were washed with water (3x5ml), acetone (2x2ml) and pentane (2x5ml) and recrystallized with benzeneligh Petroleum (1:1V1V).

**[Rh NO(NO<sub>2</sub>)<sub>2</sub> (ETH)<sub>2</sub>]**

To a continuously stirred suspension of [Rh NO(NO<sub>2</sub>)<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub>] (0.19g, 0.25mmol) in THF (10ml) was added 2 equivalent (0.1g, 0.50mmol) of ETH and resultant mixture was further stirred to then filtered. On adding petroleum ether (60-80°C) to the filtrate on yellow precipitate of the complex was formed. It was filtered and washed with petroleum ether (2x2ml) and ether (2x2ml) and dried in vacuo.

**[Rh NO (Cl<sub>2</sub>) (PTH)<sub>2</sub>]**

A suspension of [Rh NO Cl<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub>] (0.18g, 0.25mmol) and 2 equivalent of PTH (0.12g, 0.50mmol) in 20ml THF was heated of reflux for 2-3h, during which the colour changed from light brown to orange brown. The solvent was pumped off and residue was washed with Et<sub>2</sub>O and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O-hexane afforded orange brown crystals.

**[Rh NO(Br<sub>2</sub>) (PTH)<sub>2</sub>]**

A suspension of [Rh NO(Br<sub>2</sub>) (PPh<sub>3</sub>)<sub>2</sub>] (0.20g, 0.25mmol) and 2 equivalent of PTH (0.12g, 0.50mmol) in THF- acetone (20ml, 1:1V1V) was heated under reflux for 5min during which the colour of solution change from orange brown to red brown. It was filtered and concentrated to 5ml and Rept in refrigerator for 1h during which the red brown crystals of complex separated. It was filtered, washed with ethanol (1x1ml), acetone (1x1ml), ether (1x1ml) and dried in vacuo.

**[Rh NO(I<sub>2</sub>) (PTH)<sub>2</sub>]**

An excess of lithium iodide (0.15g) was added to the solution of dichoronitrosyl rhodium (I) (0.05g) in acetone (5ml) and the mixture was shaken for 1h. The excess of PTH (0.15g) in 10ml ethanol- dichloromethane (1:1V1V) was slowly added and the reaction mixture was stirred for 1h then heated to reflux for 5min. The violet brown crystals which separated were washed with water (3x5ml), acetone (2x2ml), and pentane (2x5ml) and recrystallized from benzeneligh petroleum.

**[Rh NO (NO<sub>2</sub>)<sub>2</sub> (PTH)<sub>2</sub>]**

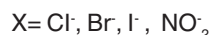
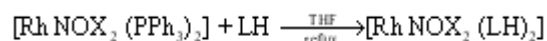
A suspension of [Rh NO (NO<sub>2</sub>)<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub>] (0.19g, 0.25mmol) and 2 equivalent of PTH (0.12g, 0.50mmol) in THF (25ml) was stirred for 5h and heated to reflux for 30 min then filtered. The solution was concentrated to 5ml under reduced pressure and Kept in referigerator for 1h where by a pale yellow crystalline complex was separated. It was filtered and washed with (1x1ml) THF (1x1ml) CH<sub>2</sub>Cl<sub>2</sub>, (1x1ml) Et<sub>2</sub>O and dried in vacuo.

**Analyses**

Rhodium and Sulphur were estimated by started procuder Corbon, hydrogen and nitrogen analyses were performed by the microanalytical section of B.H.U. Varanasi. The analytical results are given in Table. I.R spectra were recorded on PerRin- Elemer Model 580 in KBr Disc. The IR spectral data are given Table. U.V, Visible spectra of the ligand and complexes were recorded on cystronic Model 108 and the data are given in Table magnetic properties of the complexes were determined on Gouy balaue at room temperature.

**RESULTS AND DISCUSSION**

Treatment of [Rh NOX<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub>] with LH, ETH or PTH in THF aforded [Rh NOX<sub>2</sub> (LH)<sub>2</sub>] air stable crystalline compounds.



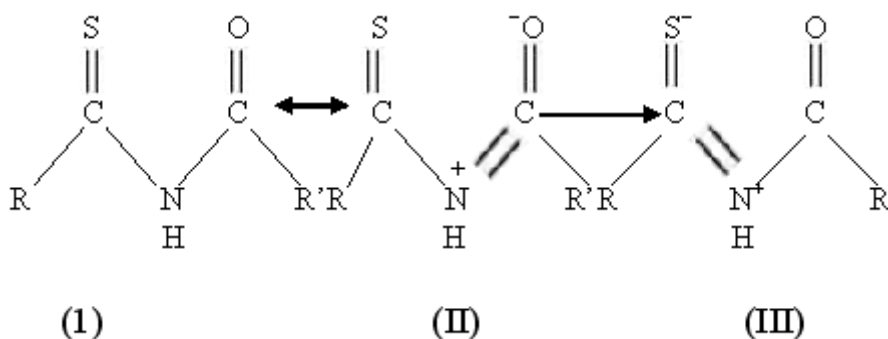
The IR NO stretching frequency 1635-1660 Cm<sup>-1</sup> for the compounds (1-8) are within the range of expected for bent nitrosyl compound.<sup>1</sup>

Although they are higher than that for  $[\text{Rh}(\text{NOX}_2(\text{PPh}_3)_2)]$   $1560\text{ cm}^{-1}$ . This suggests that  $\text{PPh}_3$  ligand is stronger donor than sulphur counterpart. Further, the stretching frequencies of NO in a given series of compounds  $[\text{Rh}(\text{NOX}_2(\text{ETH})_2)]$  are found to reduce in the order  $\text{NO}_2^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$ . The larger  $\pi$ -donor ability of the ligand X causes a smaller  $\nu(\text{NO})$ .

Attempts have been made to activate the nitrosyl ligand of the Rh nitrosyl. Compound by treatment with nucleophiles and electrophiles. NO reactions were found when  $[\text{Rh}(\text{NO})\text{X}_2(\text{LH})_2]$  were reacted with MeLi or  $\text{LiEtEt}_3\text{H}$ . The position of nitrosyl

band  $\nu(\text{NO})$  the IR spectra of  $[\text{Rh}(\text{NO})\text{X}_2(\text{LH})_2]$  is not affected ( $< 20\text{ cm}^{-1}$ ) by change of the medium from KBr to  $\text{CH}_2\text{Cl}_2$  solution and we therefore, conclude that essentially the same molecular structure prevails for these complexes in the solid state and solution. However, splitting of the nitrosyl band observed in some of the solid state spectra, and tentatively attributed to solid state effects, are absent from the corresponding solution spectra.

The title ligand LH is capable of existing (I, II and III) in three tautomeric forms and clearly possesses a variety of coordinating possibilities.



R=2-Phyrrolyl, R'=OEt; N-Ethoxycarbonylpyrrole-2-thiocarboxamide(ETH).  
R=2-Phyrrolyl, R'=NHPh; N-Phenylcarbomoylpyrrol-2-thiocarboxamide(PTH).

The eventual outcome of a particular interaction will be decided by the character of acceptor cation, the reaction conditions as well as other factors which are known to effect the behavior of the ambidentate ligands<sup>5</sup>. Free ligand exists as I but II and III forms do become operative when the ligand gets coordinated to the metal ions<sup>6,7</sup>.

The nitrogen atom of Pyrrole ring is not capable to coordinate to metal ion under the reaction condition. The proton of the NH group can be ionized to get uninegative ligand in presence of highly basic medium but under this condition ligand is converted to pyrrole-2-thiocarboxamide. N and O/N or O of  $\text{RCSNHCOR}'$  moiety will prefer to coordinate more effectively with hard Lewis acids (Metal ion) in series of complexes  $[\text{RhNOX}_2(\text{PPh}_3)_2]$  (X= Cl, Br, I,  $\text{NO}_2^-$ ), Rh is present in +3 state,  $\text{Rh}^{+3}$  is a border line Lewis acid, which may prefer to bind the ligand through N, O or S side. Thus, in order to know the mode of

linkage of ligand, the IR spectrum of ligand and complexes were compared. Followings are the result of IR spectral studies.

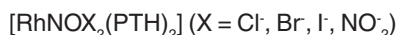
#### $[\text{RhNOX}_2(\text{ETH})_2]$ (X= Cl, Br, I, and $\text{NO}_2^-$ )

- (1) Characteristic bands of pyrrole ring<sup>9</sup> ( $3340, 1550, 1470, 1400, 1140, 1040, 995, 890$  and  $750\text{ cm}^{-1}$ ) were not shifted in the spectra of complexes (maximum shift  $\pm 5\text{ cm}^{-1}$ ), suggesting that NH group of pyrrole ring is not participating in the bond formation.
- (2) The band due to  $\nu(\text{NH})$  and  $\delta(\text{NH})$  ( $3360, 3145, 630$  and  $600\text{ cm}^{-1}$ ), The amide band I at  $1775\text{ cm}^{-1}$  and  $\nu(\text{C-OEt})$  band at  $1190\text{ cm}^{-1}$  did not shift in the spectra of complexes, indicating no bond formation with NH and CO group.
- (3) The thioamide bands<sup>10-12</sup> I ( $\delta(\text{C-H}) + \delta(\text{N-H}) + \nu(\text{C=N})$ ); II ( $\nu(\text{C=S}) + \nu(\text{C=N}) + \delta(\text{N-H})$ ); III ( $\nu(\text{C-N}) + \nu(\text{C-S})$ ), and IV ( $\nu(\text{C-S})$ ) modes of



- vibrations of ligand appearing at 1540, 1340, 1070 and 870  $\text{cm}^{-1}$  respectively, undergo blue shift of the band I(10-15) $\text{cm}^{-1}$  and red shift (20-25 $\text{cm}^{-1}$ ) of the band II-IV, indicating the coordination of the ligand through Sulphur atom.
- (4) The characteristic<sup>13</sup> bands of  $\text{NO}_2$  at 1346  $\text{cm}^{-1}$  as  $\nu(\text{NO}_2)$  and 1330  $\text{cm}^{-1}$  as  $\nu_s(\text{NO}_2)$  were present in corresponding nitro complexes.
  - (5) The weak intersits bands at 325-270 $\text{cm}^{-1}$  appeared in the IR spectra of  $[\text{RhNOX}_2(\text{ETH})_2]$  are assigned to  $\nu(\text{Rh} - \text{x})$ . The Stretching frequency of these bands increases in the order  $\text{I}^- < \text{Br} < \text{Cl}^- < \text{NO}_2^-$ .
  - (6) The IR Spectra of  $[\text{RhNOX}_2(\text{ETH})_2]$  show broad bands at 1635-1660  $\text{cm}^{-1}$ . The position of these bands depend upon nature ligand x. These bands are assigned to  $\nu(\text{NO})$ <sup>14</sup>.
  - (7) The medium intensity band appeared at 350-480 $\text{cm}^{-1}$  in spectra of all the complexes are assigned to  $\nu(\text{Rh} - \text{S})$ .

The Systematic assignments of all the bands are given in Table.



On Comparing the stoichiometrixes of these complexes with Known preferences of Rh(III) for coordination number five, it appears that ligand PTH is acting as unidentate. As a consequence of having five potential donor sites in the ligand molecules, these arises a number of possibilities of bond formation with metal ion. The study of IR spectrum of ligand and Nu complexes provided a possible mode of linkage.

The IR spectra of the ligand and complexes were quite complicated owing to strephing and bonding vibration of CN, CH, CC, NH and CS groups. Further, the  $\nu(\text{NO})$  also appears in the region of these groups. However, the systematic shift of few bands can be used to decide the mode of linkage of ligand to the metal ion. There in a gross similarity in the spectra of all the complexes except a little change in the position of  $\nu(\text{NO})$ , suggesting that the ligand has same mode of bonding. The systematic shifts of the mejour bands and their assignments are discussed below.

- (1) The characteristic bands of pyrrole moiety

were not shifted in the spectra of complexes (maximum shift  $\pm 5\text{cm}^{-1}$ ), suggesting that NH of the pyrrole ring is not participating in the bond formation.

- (2) The bands due to  $\nu(\text{NH})$  present at 3410, 3260 and 3160  $\text{cm}^{-1}$  in the spectrum of ligand were present in those of complexes in slightly shifted position ( $\pm 5\text{cm}^{-1}$ ).
- (3) The amide bands<sup>15</sup> I at 1720  $\text{cm}^{-1}$  remained practically stationary in the spectra of all the complexes (maximum shift  $\pm 5\text{cm}^{-1}$ ).
- (4) The weak band due to  $\nu(\text{NH})$  at 630 and 680 $\text{cm}^{-1}$  did not shift.
- (5) The band due to  $\nu(\text{C} = \text{S})$ <sup>16</sup> at 860 $\text{cm}^{-1}$  shifted to the lower wave number (25 $\text{cm}^{-1}$ ) indicating the bonding of the metal ion with thiocarbonyl sulphur.
- (6) These in no systematic shift; in the position of the bands 1590-1200 $\text{cm}^{-1}$ . Since these bands arise due to modes of vibrations having contributions from  $\nu(\text{C} = \text{N})$ ,  $\delta(\text{NH})$ ,  $\nu(\text{C} = \text{C})$ ,  $\nu(\text{C} = \text{O})$ , the mixing pattern in these bands will be different from those present in the spectrum of ligand and hence one should expect a non systematic shift in the positions of these bands.
- (7) The new bands appeared in the spectra of complexes around 350  $\text{cm}^{-1}$  is assigned to  $\nu(\text{Rh-S})$ .
- (8) The characteristic bands of  $\text{NO}_2$  ( $\nu$  as  $\nu(\text{NO}_2)$  and  $\nu_s$  as  $\nu_s(\text{NO}_2)$ ) were present at 1346 and 1330  $\text{cm}^{-1}$  respectively.
- (9) All the complex  $[\text{Rh NOX}_2(\text{PTH})]$  exhibit bands from 270-330  $\text{cm}^{-1}$  which is assigned to  $(\nu\text{Rh} - \text{X})$  modes of vibration. The energy of these bands increases in the order  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_2^-$ . The systematic assignments of all these bands are given is Table.

### Electronic Spectra

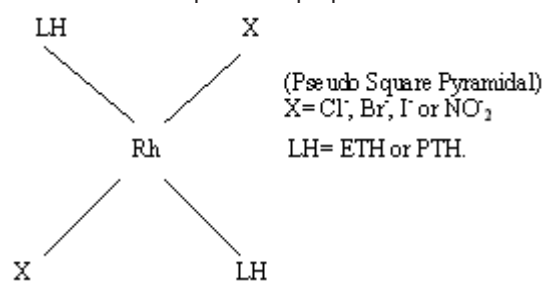
The electronic spectrum of the chloroform solution of ETH showed two absorption bands at 365 nm (S) and 440 nm(W). These bands are assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition respectively. The reasons for assigning 440nm bands to  $n \rightarrow \pi^*$  transition are (a) usually  $n \rightarrow \pi^*$  transitions involving sulphur and nitrogen atom occur at lower energy are less interse than  $\pi \rightarrow \pi^*$  transitions<sup>17, 18</sup>. The nature and positions of these band is solvent dependent. The band is absent from the spectra of

Zinc and silver complex. This may be owing to the stabilization of the energy of the lone pairs of the electron on complex formation. The electronic spectrum of the chloroform solution of the ligand PTH exhibited three bands at 415, 390 and 360 nm respectively. These bands are assigned to  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$  and CT band respectively.

The electronic spectra of complexes were taken in  $\text{CH}_2\text{Cl}_2$  from 200 to 900nm. These absorption bands were compared with the ligands absorption bands. The ligand bands at 440 and 415nm in ETH and PTH respectively disappeared owing to the stabilization of lone pair of electrons on complex formation one intense band around 400nm present in all the complexes is assigned to  $d\pi(\text{Rh}) \rightarrow \pi^*(\text{NO})$  transition, indicative<sup>19-21</sup> of  $\{\text{RhNO}\}^7$ . Rh (III) being  $d^6 (t_2g)^6$  system<sup>22-24</sup> can show four d-d transition bands corresponding to  ${}^1A_{1g} \rightarrow {}^3T_{1g}$ ,  ${}^3T_{2g}$ ,  ${}^1T_{2g}$  and  ${}^1T_{1g}$ . The two bands  ${}^1A_{1g} \rightarrow {}^3T_{1g}$  and  ${}^3T_{2g}$  are spin forbidden so they generally do not appear in electronic absorption spectrum of Rh

(III) complexes. But the two spin allowed transitions, corresponding to  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  and  ${}^1T_{1g}$  are expected to appear. But, due to presence of intense charge transfer bands the one corresponding to  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  is masked and other band ( ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ) of weak intensity at 450-470nm appear in all the complexes. The systematic assignments of these absorption bands are given in Table.

All the compounds are diamagnetic. Thus, on the basis of analytical, spectral (IR, UV and visible) and magnetic studies, the following structure<sup>25</sup> of complexes is proposed.



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