



Reactions of 2-thioxoper Hydro-1, 3-thiazin-4 ones with Cyclopentadienyl – Ruthenium II, Dicarbonyldichloro Ruthenium II Complexes and Tetra Carbonyldi- μ -Halodirhodium

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ABSTRACT

In this paper, the reaction of 2-thioxoperhydro-1, 3-thiazine-4 ones with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{X}]$ (X=Cl, Br, I), $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MPh}_3)_2\text{Cl}]$ (M = As, Sb) and $[\text{Ru}(\text{CO})_2\text{Cl}_2]$ complexes lead to the formations of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{TPH})\text{X}]$ (X=Cl, Br, I), $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MP}\eta^3)(\text{TPH})\text{Cl}]$ (M=As, Sb) $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{TPH})]$ and $[\text{Rh}(\text{CO})_2\text{X}(\text{TPH})]$ (X=Cl, Br) The compounds have been characterised by analytical, magnetic, conductivity and spectroscopic (ir, uv and visible) studies and a quasioctahedral geometry is proposed for Ru(II) complexes and square planar geometry for Rh(I) Complexes.

Key words: Spectroscopic methods, quasioctahedral geometry, Ruthenium complexes.

INTRODUCTION

It is recognised that the properties of the metal complexes of phosphorus donor ligands^{1,3} are markedly affected by the electronic and steric effects of the substituents on Phosphorus. However, investigations on the electronic and steric effects in metal complexes of arsenic donor ligands have been lacking. Recently reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$ with source aromatic thioamides ($\text{R}_1\text{CSNHCOR}_2$) have been reported⁴. We report here the synthesis and characterisation of the products of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{X}]$ (X=Cl, Br, I), with

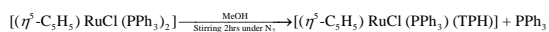
TPH & $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MPh}_3)_2]$ (M = As, Sb) and $[\text{Rh}(\text{CO})_2\text{X}]$ and $[\text{Ru}(\text{CO})_2\text{X}]$ (X=Cl, Br, I), with TPH respectively.

EXPERIMENTAL

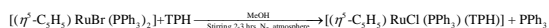
All the chemicals used were either of AR or chemically pure grade 2 – Thioxoperhydro-1, 3-thiazine-4 ones, (TPH) was prepared by the literature method given elsewhere⁵ $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{X}]$ (X=Cl, Br, I),⁶ $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MP}\eta^3)_2\text{Cl}]$ ^{7,8} (M = As, Sb), $[\text{Ru}(\text{CO})_2\text{Cl}_2]$ ⁹ and $[\text{Rh}(\text{CO})\text{X}]_2$ ^{10,11} were prepared by literature methods.

Preparation of metal Complexes **$[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2](\text{TPH})$**

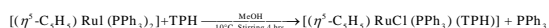
A solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2]$ (0.182g, 0.25 mmol) and ligand TPH (0.52g ~ 0.35 mmol) in 40 ml MeOH was stirred for 2hrs under a dry N_2 atmosphere. The resultant solution was kept in refrigerator for 2 hrs where by a yellowish brown crystalline complex precipitated. It was centrifuged, washed with MeOH, ether and dried in vacuo.



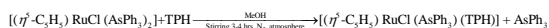
To a 20ml MeOH suspension of $[\eta^5\text{-C}_5\text{H}_5\text{RuBr}(\text{PPh}_3)_2]$ (0.19 ~ 0.25 mmol) was added MeOH solution (20ml) of ligand (0.05 ~ 0.35 mmol) with constant stirring under dry N_2 . The stirring was continued for 2-3 hrs. whereby the colour of solution changes from orange to orange brown. It was filtered and filtrate was kept in refrigerator for 2 hrs, an orange brown needle like crystal separated out. It was centrifuged, washed several times with MeOH ether and dried in vacuo.



To a 20 ml (CH_2Cl_2) solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuI}(\text{PPh}_3)_2]$ (0.20g ~ 0.25 mmol) was added drop wise 20 ml MeOH solution of ligand (0.50g ~ 0.35 mmol) with constant stirring at 10°C under a dry N_2 atmosphere. The stirring was continued for 4 hrs whereby a reddish violet crystalline complex separated. It was centrifuged, washed with methanol, dichloromethane, ether and dried in vacuo.



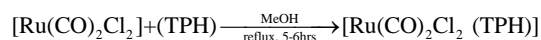
A solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{AsPh}_3)_2]$ (0.105g ~ 0.25 mmol) and ligand (0.5g ~ 0.35 mmol) in 40 ml was stirred for 2-3 hrs under a dry N_2 atmosphere. The resulting solution was evaporated to near dryness the residue extracted by CH_2Cl_2 and the complex was precipitated by using petroleum ether (60-80 $^\circ$). It was centrifuged and purified by recrystallization from CH_2Cl_2 – Petroleum ether (60-80 $^\circ$). It was again centrifuged and washed with petroleum ether and dried in vacuo.



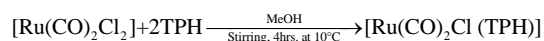
To a continuously stirred 20 ml MeOH solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{SbPh}_3)_2]$ (0.100 ~ 0.19 mmol) was added dropwise a 20 ml (MeOH) solution of ligand (0.05g ~ 0.35 mmol) at room temperature under dry N_2 atmosphere. The stirring was continued for 2-3 hrs where by the colour of reaction changes to reddish brown. It was filtered and the filtrate was kept in refrigerator for 4 hrs where by a reddish brown needle like crystals of the complex separated. It was centrifuged, washed with MeOH, ether and dried in vacuo.



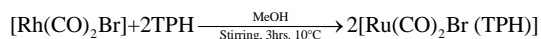
A MeOH solution (50ml) containing $[\text{Ru}(\text{CO})_2\text{Cl}_2]$ (0.114g ~ 0.5 mmol) and ligand (0.75g ~ 0.5 mmol) was refluxed for 5-6 hrs. The resulting solution was concentrated almost to dryness under reduced pressure, The residue was dissolved in minimum quantity of CH_2Cl_2 followed by an addition of excess (50ml) petroleum ether with constant stirring. On standing for 1-2 hrs, the precipitate settled. It was centrifuged, washed several times with petroleum ether (60-80 $^\circ$) and dried in vacuo.



A MeOH solution (50ml) containing $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.18g ~ 0.5 mmol) and ligand (0.15g ~ 1 mmol) was stirred for 4 hrs at 10°C where by the colour of solution changes from red to brown. It was centrifuged and centrifugate was reduced to 20 ml at low pressure and kept in refrigerator for 2 hrs where by a crystalline reddish brown compound was formed. It was centrifuged and washed with methanol, ether and dried in vacuo.



A MeOH solution (50ml) containing $[\text{Rh}(\text{CO})_2\text{Br}]_2$ (0.23 g ~ 0.5 mmol) and ligand (0.15g ~ mmol) was stirred for 3 hrs at 10°C whereby the colour of reaction mixture changes from dark brown to yellowish brown. It was centrifuged and the centrifugate was reduced to 10 ml at low pressure. On adding 50 ml petroleum ether (60-80 $^\circ$) a yellowish brown precipitate of complex was formed. It was centrifuged and washed with MeOH, ether and dried in vacuo.



Analyses

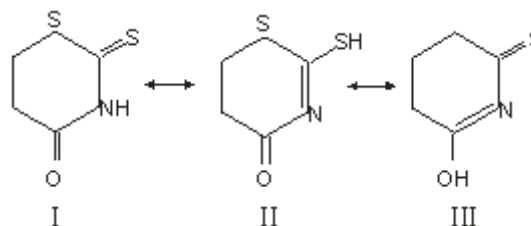
A weighed amount of complex was taken in a pyrex beaker. It was decomposed by digesting it with aquaregia for some time until the residue gave the transparent solution. The solution was used for the estimation of sulphur. Halogens were estimated by standard procedures given elsewhere¹² as $\text{Agx}(\text{X}=\text{Cl}, \text{Br}, \text{I})$. P, As, and Sb were estimated first by decomposing samples with Na_2O_2 , Sugar and NaNO_3 in a Parr Bomb, extracted the melt with water and heated it to remove SO_3 fumes. It was diluted with water and filtered. The filtrate was used to estimate P, As and Sb, by the standard procedures. Rhodium was estimated by the standard procedure¹³ C, H, N analyses were performed by the Microanalytical section of B.H.U., Varanasi, Magnetic susceptibilities of the complexes were determined with the help of Gouy balance at room temperature. IR spectra of the complexes were scanned on Perkin-Elmer spectrophotometer model 580. Melting points of the complexes were observed on Fisher-John melting points apparatus and reported without further correction. Conductivity of the complexes were checked by Elco Model apparatus.

RESULTS AND DISCUSSION

Analytical data are consistent with stoichiometry proposed for the complexes (Table-1). The compounds are non-conductors in dichloromethane, generally air stable and soluble in most of the organic solvents and are diamagnetic. In order to propose a probable structures of the complexes according to proposed formulations, the spectral (ir and uv – visible) studies have been carried out on this complexes whose results are discussed under the following heads.

IR spectral studies $[(\eta^5\text{-C}_5\text{H}_5) \text{RuX}(\text{PPh}_3)_2(\text{TPH})]$ (X=Cl, Br, I) and $[(\eta^5\text{-C}_5\text{H}_5) \text{RuCl}(\text{MPh}_3)_2(\text{TPH})]$ (M=As, Sb)

The donor ability of this class of ligand can perhaps be best understood in terms of resonance structure given below.



Ordinarily, only structure I is considered, but II and III may predominate under certain situations. In the case of coordination of the ligand through its carbonyl oxygen atom, $\nu(\text{C}=\text{O})$ should shift to lower wave number and thioamide band I [$\delta(\text{NH} + \nu(\text{CN}))$] should shift to higher wave number. Whereas if coordination is through nitrogen atom, the thioamide band I^{14, 15} will shift to lower wave number. Thioamide band II [$\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{S}) + \delta(\text{C}-\text{H})$] and III [$\nu(\text{C}-\text{N}) + \nu(\text{C}-\text{S})$]¹¹ do not shift systematically after complexation, hence they could not be used for deciding a bonding site. Based on above criterion a bonding mode has been arrived at (Table 2). In all the complexes $\nu(\text{C}=\text{O})$ of the ligand goes to lower wave numbers after complexation, hence coordination through oxygen is likely to occur. Coordination through ring nitrogen or sulphur is unlikely as they are weakly basic. The p bonding through $\text{C}=\text{S}$, $\text{C}=\text{O}$ and $\text{C}=\text{N}$ is almost ruled out on the analogy with the bonding of similar type of ligands. The X-ray crystal diffraction of $[\text{Cu}(\text{PPh}_3)_2(\text{LH})\text{Cl}]$ shows that coordination occurs through thione sulphur¹⁶⁻¹⁸.

A new strong band at around 2350 cm^{-1} appears which is assigned to $\nu(\text{O}-\text{H})$. This shows that the coordinated ligand is in thiol form. This is further confirmed by the disappearance of $\nu(\text{NH})$, $\nu(\text{C}=\text{S})$ and thioamide band IV. The smaller value of $\nu(\text{S}-\text{H})$ in the complexes may be due to strong intermolecular hydrogen bonding. In addition a new band at 600 cm^{-1} appears in all the complexes and is assigned to $\nu(\text{C}-\text{S})$. Similar ligands are reported to be predominantly in thioketoforms in solid or solutions. However, enethiolization of thioamides may markedly be enhanced in presence of metal ions.

All the characteristic bands of PPh_3 ,¹⁹ AsPh_3 ,²⁰ SbPh_3 ,^{21,22} and $\eta^5\text{-C}_5\text{H}_5$ ($820\text{-}850 \text{ cm}^{-1}$)²³ were present in the IR spectra of complexes. The new bands in the region $350\text{-}480 \text{ cm}^{-1}$ may be

Table 1 : Analytical data, Colour, Melting points, Yield, Conductivity And Magnetic properties of complexes

Compound	Colour	Melting points (°C)	Yield %	Conduc tivity	Magnetic (B.M.)	Found Calcd (%)						
						C	H	N	S	Cl/Br/I	P/As/Sb	Metal
$[\eta^5\text{-C}_5\text{H}_5] \text{RuCl} (\text{PPh}_3) (\text{TPH})]$	Yellowish brown	130	38	50.8	D	52.95 (53.07)	4.22 (4.12)	2.19 (2.29)	10.59 (10.49)	5.70 (5.80)	4.99 (5.07)	16.40 (16.54)
$[\eta^5\text{-C}_5\text{H}_5] \text{RuBr} (\text{PPh}_3) (\text{TPH})]$	Orange brown	105	60	48.4	D	49.35 (49.47)	3.96 (3.84)	2.03 (2.13)	9.88 (9.78)	12.8 (12.19)	4.60 (4.72)	15.30 (15.42)
$[\eta^5\text{-C}_5\text{H}_5] \text{RuI} (\text{PPh}_3) (\text{TPH})]$	Reddish violet	90	85	8.2	D	46.06 (46.16)	3.69 (3.58)	1.88 (1.99)	9.24 (9.13)	17.99 (18.07)	4.21 (4.41)	14.30 (14.39)
$[\eta^5\text{-C}_5\text{H}_5] \text{RuCl} (\text{PPh}_3) (\text{TPH})]$	Violet	115	42	45.6	D	49.43 (49.54)	3.19 (3.08)	2.04 (2.14)	9.90 (9.80)	5.31 (5.41)	11.30 (11.45)	15.34 (15.44)
$[\eta^5\text{-C}_5\text{H}_5] \text{RuCl} (\text{SbPh}_3) (\text{TPH})]$	Grey	105	35	24.5	D	46.10 (46.20)	2.92 (2.87)	1.87 (1.99)	9.26 (9.14)	4.96 (5.05)	17.23 (17.35)	14.30 (14.40)
$[\text{Rh}(\text{CO})_2 \text{Cl}_2 (\text{TPH})]$	Red brown	200	66	30	D	19.10 (19.21)	1.46 (1.34)	3.63 (3.73)	17.20 (17.10)	18.80 (18.90)	-	26.86 (26.95)
$[\text{Rh}(\text{CO})_2 \text{Cl} (\text{TPH})]$	Yellowish brown	200 ^d	45	26.8	D	21.00 (21.10)	1.58 (1.47)	4.01 (4.10)	18.88 (18.78)	10.28 (10.38)	-	30.04 (30.14)
$[\text{Rh}(\text{CO})_2 \text{Br} (\text{TPH})]$	Dark brown	140	20	18.4	D	18.57 (18.67)	1.40 (1.30)	3.53 (3.63)	16.75 (16.62)	20.60 (20.71)	-	26.57 (26.67)

attributed to ν (Ru-Cl) + ν (Ru-O) in Ru (η^5 -C₅H₅) Cl (MPh₃) (TPH) (M=P, As, Sb) where as in [(Ru(η^5 -C₅H₅)X(PPh₃)) (TPH)] the new bands around 260-350 cm⁻¹ are assigned to ν (Ru-X) + ν (Ru-O)²² (X=Br, I).

[Rh(CO)₂ Cl₂ (TPH)]

The band due to ν (C=O) shifts to higher wave numbers on complexation, excluding the possibility of carbonyl oxygen as donar. The ν (C=S) band and the thioamide band IV (mainly due to n (C=S)) shift to lower wave numbers with reduced intensity. This support the bonding through thiocarbonyl sulphur. The thioamide band I (δ (NH) + ν (CN)) in complexes shift to lower wave numbers indicating metal nitrogen bond formation. Thioamide band II (ν (C=N) + δ (NH) + δ (CH)) and thioamide band III (ν (C = S) + ν (C - N)), as expected also shift

to lower wave numbers. The ligand is probably nitrogen and sulphur donor is these complexes. An intense band at 2040 cm⁻¹ is assigned to ν (C^oO). This also indicates the presence of two carbonyl ligand in the trans position.²⁵

[Rh(CO)₂ X (TPH)]

- (i) Ligand band at 3160 cm⁻¹ ν (NH) did not change its position (± 5 cm⁻¹) in the spectra of complexes. This could probably be explained on the assumption that during the formation of complexes, the NH group of the ligand is not participating in the bond formation. The bands due to \sim (NH) at 645 and 680 cm⁻¹ of the ligand were observed in the spectra of complexes without any shift (± 5 cm⁻¹).
- (ii) The band due to ν (CO)²⁶ of the ligand at 1710 cm⁻¹ shift to higher wave number by 20

Table 2 : IR Spectral Bands of Ligands and Complexes (cm⁻¹)

Compound	ν (NH)	ν (C=O)	ν (C=O)	ν (C=S)	Thioamide bands			
					I	II	III	IV
C ₄ H ₅ NOS ₂	3160m	1710s	-	1125s	1540s	1345s	1000m	750s
[(η^5 -C ₅ H ₅) RuCl (PPh ₃) (TPH)]	-	190s	-	1135s	1555s	1350s	1005s	-
[(η^5 -C ₅ H ₅) RuBr (PPh ₃) (TPH)]	-	190s	-	1130s	1560s	1355s	1015m	-
[(η^5 -C ₅ H ₅) RuI (PPh ₃) (TPH)]	-	1690s	-	1140s	1550s	1340sd	1010m	-
[(η^5 -C ₅ H ₅) RuCl (PPh ₃) (TPH)]	-	1690s	-	1130s	1560s	1340s	1020m	-
[(η^5 -C ₅ H ₅) RuCl (SbPh ₃) (TPH)]	-	1695s	-	1145s	1565s	1350s	1015m	-
[Rh(CO) ₂ Cl ₂ (TPH)]	3125m	1735s	2040s	1120s	1520s	1320s	980m	740s
[Rh(CO) ₂ Cl (TPH)]	3120m	1735s	2020s	1105s	1525s	1325s	990m	730s
[Rh(CO) ₂ Br (TPH)]	3100m	1730s	2005	1110s	1520s	1325s	975m	725s

Table 3 : Electronic Spectra of the Ligands and Complexes in CH₂Cl₂

Compound	λ_{max} (nm)	Assignments
C ₄ H ₅ NOS ₂	360s	$\pi \rightarrow \pi^*$
	450s	$\eta \rightarrow \pi^*$
[(η^5 -C ₅ H ₅) RuCl (PPh ₃) (TPH)]	355s460s	ILCT
[(η^5 -C ₅ H ₅) RuBr (PPh ₃) (TPH)]	350s450s	ILCT
[(η^5 -C ₅ H ₅) RuI (PPh ₃) (TPH)]	340s450s	ILCT
[(η^5 -C ₅ H ₅) RuCl (PPh ₃) (TPH)]	350s465s	ILCT
[(η^5 -C ₅ H ₅) RuCl (SbPh ₃) (TPH)]	350s465s	ILCT
[Rh(CO) ₂ Cl ₂ (TPH)]	340450	-
[Rh(CO) ₂ Cl (TPH)]	335440540605	ILCT ¹ A ₂ g \rightarrow ³ T ₂ g ¹ A ₂ g \rightarrow ³ B ₁ g
[Rh(CO) ₂ Br (TPH)]	340450540605	ILCT ¹ A ₂ g \rightarrow ³ T ₂ g ¹ A ₂ g \rightarrow ³ B ₁ g

- cm⁻¹. This indicates the non involvement of carbonyl oxygen in the bond formation with the metal ion.
- (iii) The ν (C=S) of the ligand at 1125 cm⁻¹ and at 750 cm⁻¹ (thioamide band IV) shift to lower frequencies (20-25 cm⁻¹).
 - (iv) The band at 1500 cm⁻¹ in the ligand is assigned to thioamide band I (ν (C=N) + δ (C - H)). In most of the complexes this band shift to higher wave numbers (Table 2).
 - (v) The ligand band at 1345 cm⁻¹ assigned to thioamide band II (ν (C=S) + ν (C - N) + δ (C - N)), shifts to lower frequencies (10-12 cm⁻¹) in the spectra of complexes.
 - (vi) The thioamide band III (mainly due to (ν (C=S) and ν (C - N))) at 1000 cm⁻¹ undergoes downward shift (10 cm⁻¹) an complexation.
 - (vii) The appearance of an intense band at 1960 cm⁻¹ [Rh(CO)₂ Cl (TPH)] and 1940 cm⁻¹ in [Rh(CO)₂ (Br) (TPH)] indicates the presence of carbonyl groups in trans position in both the complexes.²⁵
 - (viii) Two new bands at 300-350 cm⁻¹ in chloro complex may be assigned to coupled vibration of ν (Rh-Cl) and ν (Rh-S). In bromo complex the bands at 260-320 cm⁻¹ may be similarly assigned to ν (Rh-Br) + (Rh-S) vibrations.²⁴

Magnetic and uv-visible spectra of the complexes

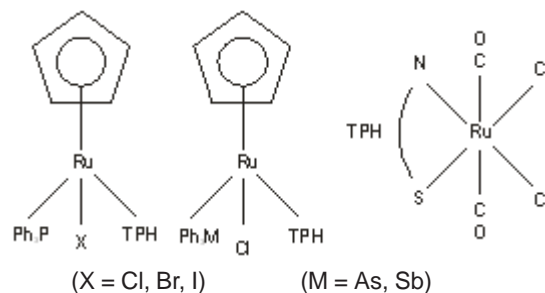
[(η^5 -C₅H₅) RuX (PPh₃) (TPH)] (X=Cl, Br, I) and [(η^5 -C₅H₅) RuCl (MPh₃) (TPH)] and [Rh(CO)₂ Cl₂ (TPH)]

All the complexes are diamagnetic in solid state. This points towards an octahedral strong field environment of ligands around metal Ru(II) ions (d⁶ system) and square planer geometry around Rh(I) ions (d⁸ system) causing a low spin configuration. Table 3 lists the λ max of the electronic spectra of the ligand and complexes obtained at room temperature in dichloromethane along with their assignments.

In visible region a rather broad band of medium intensity centering around 450 nm was exhibited by all the complexes. As it is generally believed that d-d or MLCT transition in Ru(II) octahedral complexes occur under a broad envelop at around 450 nm. The Presence of a similar band in present complexes suggested an octahedral

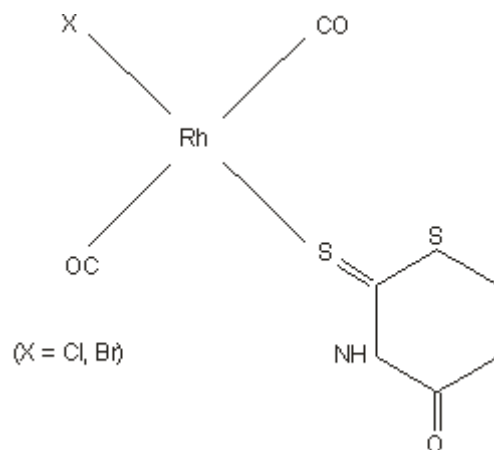
geometry of ligand around Ru(II) ion. The 450 band seems to be ligand dependent, it may be assigned to MLCT.^{28, 29} The probability of this band being due purely to d-d transition is rather low, because of the availability of low lying empty π^* orbitals of the ligand. The strong bands in all the complexes at 340-330 nm may be assigned to intraligand bands.³⁰

The conductivity at room temperature ranges from 8.3 mhos to 56.8 mhos for all the complexes (Table 1) indicating their non ionic nature³¹ in dichloromethane since no trend of conductivity with composition is evident it is probable that measured conductivities are strongly influenced by impurities. A distorted octahedral geometry is suggested for all the complexes.



In UV-visible spectrum of Rh(I) (ground state ¹A_{2g}) complex should exhibit three spin allowed and three spin forbidden bands.³² Besides these the spectrum should show three spin forbidden singlet triplet transitions from ¹A_{2g} → ³A_{2g}, ³B_{1g} and ³E_g respectively. But only two extremely weak bands are present at 540 and 605 nm. These bands are assigned to singlet to triplet transitions ¹A_{2g} → ³A_{2g}, ³B_{1g} in square planar Rh(I) complexes. The third band around 450 nm is masked by the presence of intense charge transfer band.

The conductivity of these complexes in dichloromethane at room temperature was found to be 26.8 mohms for [Rh(CO)₂Cl(TPH)] and 18.4 mohms for [Rh(CO)₂Br(TPH)] indicating their non ionic nature in dichloromethane. Thus, on the basis of analytical, conductivity and magnetic spectral (ir and uv-visible) studies, a square planer geometry is suggested for these complexes.



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