

## Spectral Studies on Hydridophosphine Complexes of Pt-Group Metals: Part-III

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Mixed-ligand hydridophosphine complexes of Ru(II) and Pt(II) with 1-*p*-tolyl tetrazoline-5-thione have been prepared and characterized using various physico-chemical studies. Hydridophosphine complexes of Pt(II) are prepared by oxidative addition to Pt(O)-compounds with inorganic acids. Tentative structures are assigned using UV-vis, IR, <sup>1</sup>H NMR and other physico-chemical measurements.

**Key Words:** Hydridophosphine complexes, Pt-group metals. Heterocyclic thioamide.

### INTRODUCTION

Hydridophosphine complexes of transition metals are reviewed by several workers<sup>1-4</sup>. The present paper describes preparations and spectral characterization of some mixed-ligand hydridophosphine complexes of Ru(II) and Pt(II) with 1-*p*-tolyl tetrazoline-5-thione in continuation of our previous report<sup>5-7</sup>.

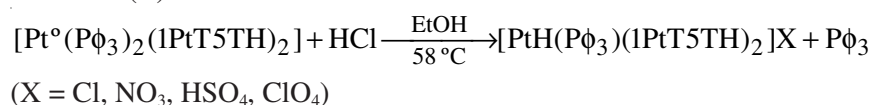
### EXPERIMENTAL

All chemicals used were of AR grade or Cp grade. 1-*p*-tolyl tetrazoline-5-thione was prepared by the method of Lieber *et al.*<sup>8</sup> Hydridophosphine complexes of Pt(II) were prepared using precursor complex [Pt(Pφ<sub>3</sub>)<sub>2</sub>(1PtT<sub>5</sub>TH)<sub>2</sub>]<sup>9</sup> and 15 % ethanolic solution of inorganic acids in appropriate molar ratio. Hydridophosphine complexes of Rh(II) were prepared by the displacement reaction between [RuH(CO)Pφ<sub>3</sub>]<sub>3</sub>Cl<sup>10</sup> and ligand in benzene as our earlier report<sup>5</sup>.

Elemental analyses, magnetic moment, conductometric, IR, UV-vis, <sup>1</sup>H NMR spectra were obtained as our previous report<sup>11</sup>.

### RESULTS AND DISCUSSION

The coordinative unsaturated species [Pt<sup>0</sup>(Pφ<sub>3</sub>)<sub>2</sub>(1PtT<sub>5</sub>TH)<sub>2</sub>] display oxidative addition reaction with ethanolic inorganic acids to form colourless and diamagnetic hydrides of Pt(II) as below:



Molar conductance value in DMF (Table-1) is in agreement with required by a uni-univalent electrolyte<sup>12</sup>. The low value of molar conductance may be due to large ions. It seems that these anions have low coordinating power to form ionic hydrides and present in the outer sphere of complexes. Chatt *et al.*<sup>13</sup> have suggested that ions like CN<sup>-</sup> and SCN<sup>-</sup> have high coordinating power and affords covalent compounds during oxidative addition of Pt(O)-complexes. The presence of ionic chloride, nitrate, bisulphate and perchlorate was further supported by chemical analysis of sodium extrate solution of complexes and infrared spectra. Hydrido-phosphine complexes of Ru(II) are diamagnetic and non-conducting indicating  $d^6$ -configuration of divalent ruthenium in strong octahedral crystal field.

TABLE-1  
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Complex	Colour	Molar cond <sup>a</sup> ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )	Analysis % Found./(Calcd.)			
			C	H	N	M
[RuH(CO)(P $\phi_3$ ) <sub>2</sub> (LH)Cl]	Light brown	nc	61.35 (61.21)	4.41 (4.42)	6.44 (6.43)	11.81 (11.52)
[RuH(CO)(P $\phi_3$ )(LH) <sub>2</sub> Cl]	Yellow	nc	52.01 51.71	4.01 (3.93)	13.88 (13.78)	12.56 (12.52)
[PtH(P $\phi_3$ )(LH) <sub>2</sub> ]Cl	White	25.25	46.32 (46.49)	3.65 (3.64)	13.10 (12.76)	22.56 (22.22)
[PtH(P $\phi_3$ )(LH) <sub>2</sub> ]NO <sub>3</sub>	Light yellow	27.23	45.32 (45.16)	3.43 (3.53)	14.12 (13.93)	21.81 (21.57)
[PtH(P $\phi_3$ )(LH) <sub>2</sub> ]HSO <sub>4</sub>	White	30.21	43.32 (43.45)	3.61 (3.51)	12.01 (11.92)	21.01 (20.76)
[PtH(P $\phi_3$ )(LH) <sub>2</sub> ]ClO <sub>4</sub>	White	28.31	43.12 (43.33)	3.40 (3.39)	12.01 (11.89)	20.82 (20.71)

LH = 1-*p*-tolyltetrazoline-5-thione.

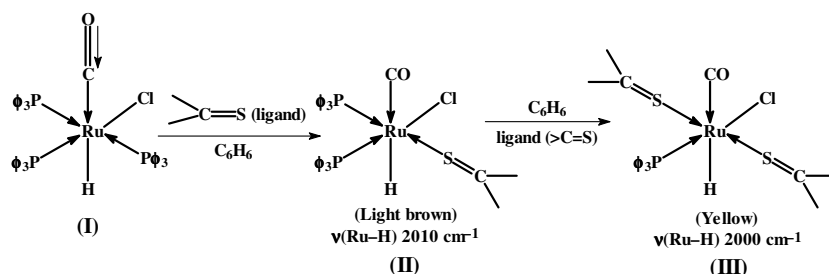
The diamagnetism exhibited by the Pt(II) complexes is indicative their low spin square planar configuration. The reflectance spectra of complexes display band in 27770-24390  $\text{cm}^{-1}$  region assignable to  $^1A_{1g} \rightarrow ^1B_{1g}$  transition in square planar field<sup>14</sup>. The other ligand field bands are obscured by strong CT band observed at 47000  $\text{cm}^{-1}$ . It seems high degree of *d-p* mixing in the complexes.

The diamagnetism exhibited by ruthenium(II) complexes indicate  $^1A_{1g}$  ground state and two spin allowed transitions  $^1A_{1g} \rightarrow ^1T_{1g}$  and  $^1A_{1g} \rightarrow ^1T_{2g}$  are observed at 14000 and 17700  $\text{cm}^{-1}$ , respectively indicating octahedral structure<sup>15</sup>. A weak spin-forbidden transition  $^1A_{1g} \rightarrow ^3T_{1g}$  (13125  $\text{cm}^{-1}$ ) is also observed in concentrated solution. The absorption band around 28190  $\text{cm}^{-1}$  of high intensity probably due to charge transfer from ligand to metal. Thus, octahedral configuration of all Ru(II) complexes was assumed considering previous literature<sup>15-17</sup>.

**IR Spectra:** All ionic platinum(II) hydrides show an IR absorption band of medium intensity between 2050-2100  $\text{cm}^{-1}$  assigned to  $\nu(\text{Pt-H})$  and another less intense one between 830-800  $\text{cm}^{-1}$  due to  $\delta(\text{Pt-H})$  mode<sup>18</sup>. These assignments

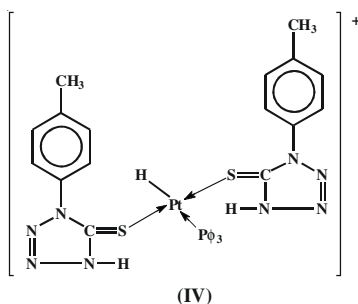
are in good agreement with criteria given by Chatt *et al.*<sup>13</sup> with *trans*-effect of  $P\phi_3$ . Church and Co-workers<sup>19</sup> found the position of Pt-H stretching frequency sensitive to *trans* ligand in square planar Pt(II) complexes and here hydrido ligand and  $P\phi_3$  group are at *trans* in planar structure (IV).

All hydridophosphine complexes of ruthenium(II) display bands at 2000-1900  $\text{cm}^{-1}$  and 740-710  $\text{cm}^{-1}$  assigned to  $\nu(\text{Ru-H})$  and  $\delta(\text{Ru-H})$ , respectively<sup>15-17</sup>. A strong broad band at 1975  $\text{cm}^{-1}$  corresponding to  $\nu(\text{C}\equiv\text{O})$  mode of coordinated carbonyl group<sup>16</sup>. The interaction between C O group and  $P\phi_3$  group is observed and the fact is substantiated by splitting of  $\nu(\text{C}\equiv\text{O})$  band in the spectra of complexes. *Trans* effect of  $P\phi_3$  is greater than that of hydride ion, the following octahedral structure of complexes may be assigned.



Thioamide bands<sup>20</sup> of 1-*p*-tolyl tetrazoline-5-thione are mixed bands observed at 1504 (s) (band I), 1286 (m) (band II), 1050 (m) (band III) and at 790 (m)  $\text{cm}^{-1}$  (band IV) undergo change in position and intensity on coordination to Pt(II) or Ru(II) ions. The coordination through thiocarbonyl sulphur leads to red shifting of band IV [ $\nu(\text{C}\equiv\text{S})$ ], band III [ $\nu(\text{C}\equiv\text{N}) + \nu(\text{C}\equiv\text{S})$ ] and band II [ $\nu(\text{C}\equiv\text{S}) + \delta(\text{NH}) + \nu(\text{C}\equiv\text{N})$ ] where as band I ( $\delta(\text{NH}) + \nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ ) remains unaffected<sup>21</sup>. The  $\nu(\text{N-H})$  band of the ligand splits on complexation and observed at higher frequency suggesting the presence of imino group and absence of bonding through nitrogen atom.

The single non-ligand band at 310  $\text{cm}^{-1}$  in far IR spectra of Pt(II) complexes indicate two thioamide ligands are at *trans*-position and assigned to platinum-sulphur stretching mode in square planar structure. New bands at 470 and 420  $\text{cm}^{-1}$  assigned to mode and at 430  $\text{cm}^{-1}$  [ $\nu(\text{Ru-Cl})$ ], 370  $\text{cm}^{-1}$  [ $\nu(\text{Ru-P})$ ], and 330  $\text{cm}^{-1}$  [ $\nu(\text{Ru-S})$ ] modes<sup>22</sup>.



The absorption associated with anions in the complexes are identified at 1095 and 610  $\text{cm}^{-1}$  for perchlorate<sup>23</sup>, 1360 and 825  $\text{cm}^{-1}$  for nitrate<sup>24</sup>, 3420, 1250-1230  $\text{cm}^{-1}$ , 1057 and 1020  $\text{cm}^{-1}$  for bisulphate<sup>12</sup> and all these correspond to their uncoordinated nature.

**<sup>1</sup>H NMR Spectra:** <sup>1</sup>H NMR spectra of ligands and complexes were recorded in  $\text{CDCl}_3/\text{TMS}$  to substantiate further bonding of ligand with metal(II) ions. The spectra of complexes display multiplets in the region  $\delta$ 6.62-7.22 ppm due to aromatic protons of  $\text{P}\phi_3$  molecule<sup>25</sup>. However, broad multiplet in the region  $\delta$  7.8-8.0 ppm for phenyl protons of 1-*p*-tolyl tetrazoline-5-thione which are in different magnetic environments. The broad nature of peak may be due to the presence of four nitrogen atoms which display large quadrupole resonance broadening effect or ligand exchange reaction in solution<sup>26</sup>. The methyl protons of ligand are observed at  $\delta$ 2.42 ppm. However, the N-H proton signal is masked by the strong and the broad signal due to phenyl protons. This is indicated by the relative area of phenyl proton peak which is greater by two units than required for phenyl protons. Thus, the N-H group of ligand is intact on complexation and coordination occurs through thiocarbonyl sulphur. These observations are consistent with the conclusion drawn from IR spectral studies.

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