

## Spectral studies on hydridophosphine complexes of Pt-group metals : Part - IV

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### ABSTRACT

Hydridophosphine complexes of Ru(II), Pd(II), Pt(II), Rh(III) and Ir(III) with ethylene thiourea have been prepared and characterised using various physico – chemical techniques. The structure of all new complexes have been assigned tentatively and ligand acts monodentate sulphur donor.

**Key words:** Mixed-ligand Hydridophosphine complexes, Pt-group Metals, Ethylene thiourea.

### INTRODUCTION

Organometallic complexes of Pt-group metals have received scarce attention due to their anti-cancer activity<sup>1-5</sup>. The present communication describes the results of physico-chemical and structural investigations on hydrido-phosphine complexes of ruthenium (II), platinum (II), rhodium (III) and iridium (III) with ethylene thiourea (ETU).

### EXPERIMENTAL

All chemical used were of CP – grade. The ligand (ETU)<sup>6</sup> and precursor complexes [Pt(Pφ<sub>3</sub>)<sub>2</sub> (ETU)<sub>2</sub>]<sup>7</sup>, [Pd(Pφ<sub>3</sub>)<sub>2</sub> (ETU)<sub>2</sub>]<sup>8</sup>, [RuH(CS) (Pφ<sub>3</sub>)<sub>2</sub> Cl]<sup>9</sup>, [Rh (Pφ<sub>3</sub>)<sub>2</sub> (ETU) Cl]<sup>7</sup>, [Ir(CO) (Pφ<sub>3</sub>)<sub>2</sub> Cl]<sup>10</sup> and [IrH(CO) (Pφ<sub>3</sub>)<sub>2</sub> (SH)Cl]<sup>11</sup> were prepared by the methods reported in literature. The palladium (II), platinum (II), rhodium (III) and iridium (III) complexes were prepared by the oxidative reaction with 15% inorganic acid using appropriate molar ratio. Elemental analyses, magnetic, conductometric, IR, UV-vis spectra were obtained as reported earlier<sup>12</sup>.

### RESULTS AND DISCUSSION

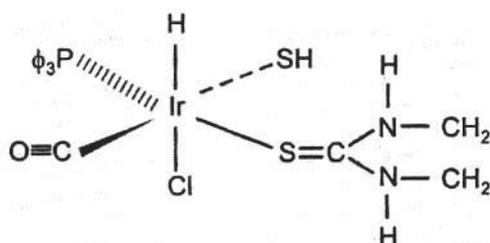
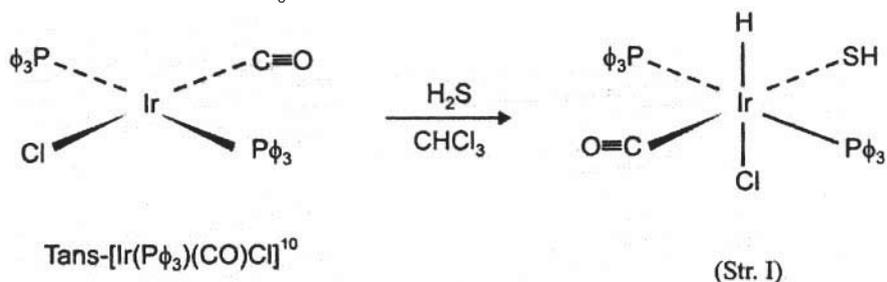
All complexes formed were stable solid at atmospheric conditions and fair soluble in DMF and DMSO. Analytical results were satisfactory and possible composition is presented in Table 1. [M<sup>o</sup>(Pφ<sub>3</sub>)<sub>2</sub> (ETU)<sub>2</sub>] (M = Pd or Pt) reacts with 15% ethanolic solution of inorganic acids and yields hydridophosphine complexes of Pt(II). But no hydrido complexes was formed by [Pd(Pφ<sub>3</sub>)<sub>2</sub>(ETU)<sub>2</sub>].



The hydride intermediate of palladium (II) are probably unstable and give [Pd(Pφ<sub>3</sub>)<sub>2</sub> (ETU)]Cl<sub>2</sub> and hydrogen. Sodium – extract of this complex produced total chlorine with AgNO<sub>3</sub> solution indicating chloride ion in outer sphere of complexes which was also supported by molar conductance value (Table 1)

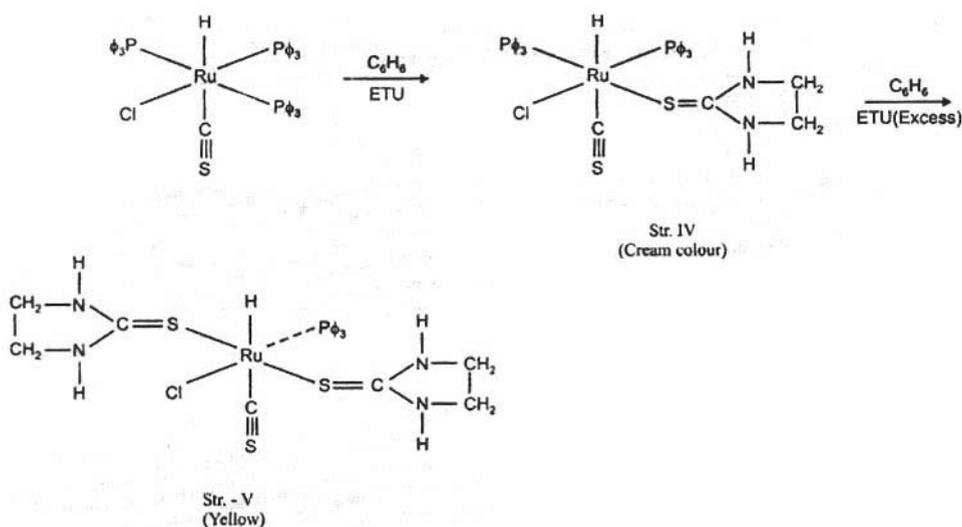
The reaction between  $\text{H}_2\text{S}$  and Trans -  $[\text{Ir}(\text{CO})(\text{P}\phi_3)_2\text{Cl}]$  in  $\text{CHCl}_3$  yields pale yellow compound  $[\text{IrH}(\text{CO})(\text{P}\phi_3)_2(\text{SH})\text{Cl}]$  (Str. 1) reported by vaska *et al.*<sup>13</sup> Further substitution with excess of ligand (ETU) yields yellow solid  $[\text{IrH}(\text{CO})(\text{P}\phi_3)(\text{ETU})$

(SH) Cl] (str. II). Iridium (III) is a 'b'-class acceptor readily forms complexes with soft sulphur donor ETU ligand and incoming ligand takes up cis-position (Str. III)



The chlorothiocarbonylhydrido tris (triphenylphosphine) ruthenium (II) undergoes ligand substitution reaction in benzene leading to

the formation of hydrido phosphine complexes of ruthenium (II) (Str. IV & V).



### Electronic spectra

The diamagnetism exhibited by the Pd(II) complexes is indicative of their low spin square-planar configuration. Electronic spectral bands Ca.  $18360\text{cm}^{-1}$  ( ${}^1A_{1g} \rightarrow {}^1A_{2g}$ )  $21240\text{cm}^{-1}$  ( ${}^1A_{1g} \rightarrow {}^1B_{1g}$ ) and  $22800\text{cm}^{-1}$  ( ${}^1A_{1g} \rightarrow {}^1E_{1g}$ ) confirms square planar stereochemistry.<sup>14</sup> The high intensity band at  $41900\text{cm}^{-1}$  is due to charge transfer. However, hydrido phosphine complexes of Pt(II) display one ligand field transition at  $\sim 23200\text{cm}^{-1}$  attributed to  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  transition similar to planar complexes<sup>15</sup>.

The ligand field bands in the Rh(III) and Ir(III) complexes are analogous<sup>16</sup> to those observed in isoelectronic Ru(II) complexes of octahedrally disposed strong ligand fields. The spectra exhibited two spin-forbidden  ${}^1A_{1g} \rightarrow {}^3T_{1g}$  ( $16644\text{cm}^{-1}$ ) and  ${}^1A_{1g} \rightarrow {}^3T_{2g}$  ( $19136\text{cm}^{-1}$ ) and two spin-allowed transitions  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  ( $23397\text{cm}^{-1}$ ) and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  ( $30232\text{cm}^{-1}$ ) for octahedral structure.<sup>17</sup> In addition to d-d transition bands one or two L → M CT band<sup>18</sup> of high intensity near  $36200\text{cm}^{-1}$  and  $40,000\text{cm}^{-1}$  are also observed in each spectrum. The absorption bands in spectrum of Rh(III) complexes (Sl. no. 9),  $21780$  and  $30760\text{cm}^{-1}$  are assigned to spin-allowed transition  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  ( $\nu_1$ ) and  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  ( $\nu_2$ ) transition and at  $13750\text{cm}^{-1}$  are probably due to spin-forbidden  ${}^1A_{1g} \rightarrow {}^3T_{1g}$  transition<sup>18</sup>. The values of ligand field parameters,  $\nu_2/\nu_1 = 1.41$ ,  $B = 560.2$ ,  $\beta = 0.77$ ,  $10Dq = 22840\text{cm}^{-1}$ , L.F.S.E. =  $27.38\text{K.Cal mol}^{-1}$  confirms distorted octahedral stereochemistry around Rh(III) ion with diamagnetic nature of complexes. The reduced value of B obtained in comparison to free-ion value ( $720\text{cm}^{-1}$ ) indicates increased covalency in metal ligand sigma bond as well as reduced effective cationic charge ( $z'$ ).

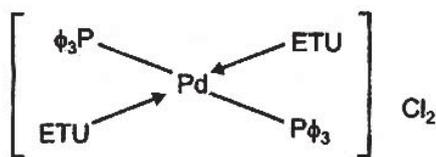
Two spin-allowed transition  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  ( $20400\text{cm}^{-1}$ ) and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  ( $18700\text{cm}^{-1}$ ) and a weak spin-forbidden transition  ${}^1A_{1g} \rightarrow {}^3T_{1g}$  ( $15125\text{cm}^{-1}$ ) are assignable to octahedral configuration of Ru(II) complexes<sup>19-20</sup>. A strong intensity band at

$30190\text{cm}^{-1}$  probably due to CT band. Ir(III) complexes also display spin-allowed two transition at  $25000\text{cm}^{-1}$  ( ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ),  $29300\text{cm}^{-1}$  ( ${}^1A_{1g} \rightarrow {}^1T_{2g}$ ) and one spin-forbidden transition at  $24100\text{cm}^{-1}$  ( ${}^1A_{1g} \rightarrow {}^3T_{1g}$ ). The value of crystal field parameters,  $\nu_2/\nu_1 = 1.17$ ,  $10Dq = 26270\text{cm}^{-1}$  and  $B = 660\text{cm}^{-1}$  consistent with octahedral structure<sup>18</sup>.

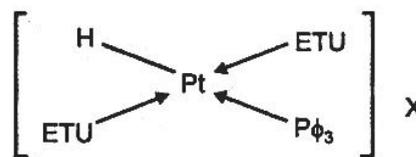
### IR Spectra

The ir spectrum of  $P\phi_3$  is recorded and interpreted by Deacon *et al*<sup>21</sup> and ETU molecule by Meek and co-workers<sup>22</sup>. Agarwala and Rao<sup>23</sup> have performed the normal coordinate analysis (N.C.A) of ETU. A comparison of the spectra of complexes with those of ETU indicate that metal-sulphur bonding results in a decrease in the frequency of thioamide band IV<sup>24</sup> by  $30-45\text{cm}^{-1}$ . The systematic change in position and intensity of other thioamide bands<sup>24-26</sup> also supports the formation of metal-S bond. Thioamide band I ( $1530\text{cm}^{-1}$ ), band II ( $1200\text{cm}^{-1}$ ) of ETU remains almost identical, Band III ( $1040\text{cm}^{-1}$ ) is either considerably lowered in intensity and/or experiences a red shift to lower frequency of the order of  $\sim 30\text{cm}^{-1}$ . The  $\nu_{\text{NH}}$  band of ETU (Ca.  $3250\text{cm}^{-1}$ ) blue shifts to higher frequency in all complexes indicating absence of bonding through imino nitrogen.

All hydridophosphine complexes of platinum(II) show an infrared absorption band of medium intensity between  $2210 - 2165\text{cm}^{-1}$  assigned to  $\nu_{\text{Pt-H}}$  and another less intense one between  $820 - 805\text{cm}^{-1}$  due to  $d_{\text{Pt-H}}$  are in agreement with the criteria suggested by Chatt *et al*<sup>27</sup>. A new weak band observed at  $585\text{cm}^{-1}$  in Pt(II) complexes and at  $580\text{cm}^{-1}$  in Pd(II) complexes are characteristics of square-planar configuration. This band is neither present in the ligand (ETU) nor in other complexes. All Pt(II) and Pd(II) complexes give rise to a doublet bands<sup>28</sup> below  $300\text{cm}^{-1}$  separated by  $10-20\text{cm}^{-1}$  due to metal-S stretching mode supports two ETU molecules at Trans-disposition in square planar structure (strs. VI & VII).



Str. VI



Str. VII

The metal – H stretching mode and bending mode of Ru(II) complexes at (2140 & 720  $\text{cm}^{-1}$ ) at 2225  $\text{cm}^{-1}$  and 810  $\text{cm}^{-1}$  for Rh(III) complexes and at 2240  $\text{cm}^{-1}$  and 790  $\text{cm}^{-1}$  for Ir(III) complexes are in agreement with previous reviews reported by Robinson *et al.*<sup>29</sup>, Pearson<sup>30</sup> and crabtree *et al.*<sup>31</sup>. The presence of single  $\nu_{\text{Ru-S}}$  (340  $\text{cm}^{-1}$ ),  $\nu_{\text{Rh-S}}$  (330  $\text{cm}^{-1}$ ) and  $\nu_{\text{Ir-S}}$  (310  $\text{cm}^{-1}$ ) band indicates two ETU molecules are at trans in octahedral structure.

The absorption associated with anions in these complexes are identified at 1350 and 820  $\text{cm}^{-1}$  for ionic nitrate<sup>32</sup>, at 1090 and 610  $\text{cm}^{-1}$  for ionic perchlorate<sup>33</sup> and at 3420, 1255 – 1230, 1050 and 1020  $\text{cm}^{-1}$  for bisulphate<sup>34</sup>, at 2525  $\text{cm}^{-1}$  for hydrosulphide<sup>35</sup> and at 339 and 325  $\text{cm}^{-1}$  for coordinated<sup>36</sup> trichlorostannate (II) ion ( $\text{SnCl}_3^-$ ). The terminal coordinated carbonyl group and thiocarbonyl group in complexes were also confirmed by the presence of non – ligand bands at 2200 -1950  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ) and at 1360 – 1290  $\text{cm}^{-1}$  ( $\nu_{\text{C=S}}$ )<sup>38</sup>.

**Table 1: Analytical and physical data of complexes.**

S. No.	Complex/(Colour, M.Pt, °C)	Mol. Cond. ( $\text{W}^{-1}\text{cm}^2\text{mol}^{-1}$ )	Analysis% Found /(Calcd)			
			C	H	N	Metal
1.	[RuH(CS) ( $\text{P}\phi_3$ ) <sub>2</sub> (ETU) Cl] (Cream, 200)	nc	59.45 (59.39)	4.66 (4.57)	3.55 (3.46)	13.41 (13.16)
2.	[Ru H(CS)( $\text{P}\phi_3$ ) (ETU) <sub>2</sub> Cl] (Yellow, > 250)	nc	46.38 (46.28)	4.33 (4.31)	8.66 (8.63)	16.00 (15.69)
3.	[Pd( $\text{P}\phi_3$ ) <sub>2</sub> (ETU) <sub>2</sub> ]Cl <sub>2</sub> (Yellow, > 250)	51.32	55.86 (55.66)	4.71 (4.63)	6.32 (6.18)	12.01 (11.75)
4.	[Pd ( $\text{P}\phi_3$ ) (ETU) <sub>3</sub> ]Cl <sub>2</sub> (Yellow, > 250)	53.32	43.86 (43.46)	4.52 (4.42)	11.36 (11.26)	14.37 (14.27)
5.	[Pt H( $\text{P}\phi_3$ ) (ETU) <sub>2</sub> ] Cl (White, > 250)	23.30	41.32 (41.29)	4.10 (4.01)	8.21 (8.02)	28.01 (27.95)
6.	[Pt H( $\text{P}\phi_3$ ) (ETU) <sub>2</sub> ] NO <sub>3</sub> (White, > 250)	24.32	39.87 (39.77)	3.80 (3.86)	9.68 (9.66)	27.01 (26.93)
7.	[Pt H( $\text{P}\phi_3$ ) (ETU) <sub>2</sub> ] HSO <sub>4</sub> (White, > 250)	21.42	38.01 (37.94)	3.81 (3.82)	7.47 (7.37)	25.81 (25.61)
8.	[Pt H ( $\text{P}\phi_3$ )( ETU) <sub>2</sub> ]ClO <sub>4</sub> (White, > 250)	19.32	37.96 (37.82)	3.68 (3.67)	7.45 (7.35)	25.80 (25.60)
9.	[Rh H( $\text{P}\phi_3$ ) <sub>2</sub> (ETU)Cl <sub>2</sub> ] (Faint yellow, 180)	nc	58.52 (58.42)	4.46 (4.49)	7.01 (6.99)	12.96 (12.86)
10.	[Rh H( $\text{P}\phi_3$ ) ( $\text{SnCl}_3$ ) (ETU) <sub>2</sub> Cl] (yellow, > 250)	nc	30.41 (30.33)	3.47 (3.37)	6.78 (6.74)	12.49 (12.39)
11.	[IrH(CO)( $\text{P}\phi_3$ ) (ETU) <sub>2</sub> (SH) Cl] (yellow, 140d)	nc	40.32 (40.37)	3.56 (3.51)	4.38 (4.28)	29.51 (29.41)
12.	(Ir H(CO) ( $\text{P}\phi_3$ )( ETU) <sub>2</sub> Cl]Cl (Yellow, > 250)	24.32	39.86 (39.56)	3.82 (3.83)	7.86 (7.66)	26.53 (26.33)
13.	[Ir H( $\text{P}\phi_3$ ) (ETU) <sub>2</sub> Cl]Cl (Yellow, > 250)	24.52	39.53 (39.43)	3.96 (3.83)	7.68 (7.66)	26.83 (26.33)

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