

Structural Studies on some Hydridophosphine and Hydridoarsine Complexes of Ruthenium (II) and Platinum (II) Ligated by Heterocyclic Thioamide

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Abstract

Some new hydridophosphine and hydridoarsine complexes of ruthenium (II) and platinum (II) have been prepared using precursor complexes $[\text{RuH}(\text{CO})(\text{E}\phi_3)_3\text{Cl}]$ and $[\text{Pt}(\text{E}\phi_3)_4]$ ($\text{E} = \text{P}/\text{As}$) without change in oxidation state of ruthenium and with change in oxidation state of platinum. The complexes are characterized using elemental analysis, electrical conductivity, magnetic measurements, IR, UV-Vis, ^1H NMR and ^{31}P NMR data. The octahedral structure to ruthenium (II) and square planar geometry to platinum (II) complexes are deduced and tentatively assigned.

Key words : hydridophosphine, hydridoarsine, Ru(II), Pt(II), Thioamide.

Introduction

Hydridophosphine complexes of transition metals are reviewed by several workers¹⁻⁴. The present paper reports Synthesis, Characterization and Structural investigation of some new hydridophosphine and hydridoarsine complexes of Ruthenium (II) and Platinum (II) with 1,2,4-triazole-3(s)-thione (tTH) in continuation of our previous report⁵⁻⁸.

Experimental

All chemicals used were of AR grade or CP grade. The ligand, 1,2,4-triazole-3(s)thione was prepared by the interaction of 1-formyl thiosemicarbazide and sodium hydroxide by the method reported in literature⁹. The precursor complexes, $[\text{RuH}(\text{CO})(\text{P}\phi_3)_3\text{Cl}]$ ¹⁰, $[\text{RuH}(\text{CO})(\text{As}\phi_3)_3\text{Cl}]$ ¹¹, $[\text{Pt}(\text{P}\phi_3)_4]$ ¹², $[\text{Pt}(\text{As}\phi_4)_4]$ ¹³ and $[\text{Pt}(\text{P}\phi_3)_2(\text{tTH})_2]$ ¹⁴ were also prepared by the

methods reported in literature.

Preparation of Ruthenium (II) Complexes:

All Ruthenium (II) complexes were prepared by the ligand substitution reaction in benzene or carbondisulphide similar to our previous method⁵.

Analysis :

Sl. No. 1 : $[\text{RuH}(\text{CO})(\text{P}\phi_3)_2(\text{tTH})\text{Cl}]$: Yellow (M. Pt = 110°C)

Calculated (%) for $\text{RuH}_{39}\text{H}_{35}\text{ON}_4\text{P}_2\text{SCL}$: C, 58.10; H, 4.34; N, 6.95; Ru, 12.59;

Found (%) : C, 58.11; H, 4.44; N, 7.01; Ru, 12.60;

Sl. No. 2 : $[\text{RuH}(\text{CO})(\text{P}\phi_3)_2(\text{tTH})_2\text{Cl}]$: Grey (M. Pt = 105°C)

Calculated (%) for $\text{RuC}_{23}\text{H}_{24}\text{N}_8\text{OS}_2\text{PCL}$: C, 41.84; H, 3.63; N, 16.98; Ru, 15.31;

Found (%) : C, 41.85; H, 3.66; N, 17.01; Ru, 15.40;

Sl. No. 3 : $[\text{RuH}(\text{CS})(\text{P}\phi_3)_2(\text{tTH})_2\text{Cl}]$: Yellow (M. Pt = 135°C)

Calculated (%) for $\text{RuC}_{23}\text{H}_{24}\text{N}_8\text{S}_3\text{PCL}$: C, 40.85; H, 3.40; N, 16.58; Ru, 14.95;

Found (%) : C, 40.89; H, 3.45; N, 16.66; Ru, 15.01;

Sl. No. 4 : $[\text{RuH}(\text{CO})(\text{As}\phi_3)_2(\text{tTH})\text{Cl}]$: Faint yellow (M. Pt = 122°C) (Decomp)

Calculated (%) for $\text{RuC}_{39}\text{H}_{35}\text{N}_4\text{OSClAs}_2$: C, 52.37; H, 3.91; N, 6.26; Ru, 11.30;

Found (%) : C, 52.47; H, 4.01; N, 6.68; Ru, 11.35;

Preparation of Platinum (II) Complexes :

The ligand substitution reaction with precursors $[\text{Pt}(\text{E}\phi_3)_4]$ (E=P/As) in dry benzene

yielded $[\text{Pt}(\text{P}\phi_3)_2(\text{tTH})_2]$ (deep yellow, M. Pt = 185°C) as we have reported earlier¹⁴. The 15% ethanolic solution of inorganic acids were refluxed with freshly prepared $[\text{Pt}(\text{P}\phi_3)_2(\text{tTH})_2]$ following our previous method⁷ to get colourless hydrido complexes of Pt (II) with 60 – 65% yield.

Analysis :

Sl. No. 5 : $[\text{PtH}(\text{P}\phi_3)_2(\text{tTH})_2]\text{Cl}$: White (M. Pt. >250°C)

Calculated (%) for $\text{PtC}_{22}\text{H}_{24}\text{N}_8\text{S}_2\text{PCL}$: C, 36.38; H, 3.30; N, 15.43; Pt, 26.87;

Found (%): C, 36.39; H, 3.40; N, 15.40; Pt, 26.88;

Sl. No. 6 : $[\text{PtH}(\text{P}\phi_3)_2(\text{tTH})_2].\text{HSO}_4$: White (M. Pt. >250°C)

Calculated (%) for $\text{PtC}_{22}\text{H}_{25}\text{N}_8\text{O}_4\text{S}_3\text{PCL}$: C, 33.54; H, 3.17; N, 14.28; Pt, 24.77;

Found (%) : C, 33.55; H, 3.18; N, 14.38; Pt, 25.01;

Sl. No. 7 : $[\text{PtH}(\text{P}\phi_3)_2(\text{tTH})_2]\text{ClO}_4$: White (M. Pt. >250°C)

Calculated (%) for $\text{PtC}_{22}\text{H}_{24}\text{N}_8\text{O}_4\text{S}_2\text{PCL}_2$: C, 33.43; H, 3.03; N, 14.18; Pt, 24.69;

Found (%) : C, 33.45; H, 3.12; N, 14.19; Pt, 24.50;

Sl. No. 8 : $[\text{PtH}(\text{As}\phi_3)_2(\text{tTH})_2]\text{Cl}$: White (M. Pt. >220°C)

Calculated (%) for $\text{PtC}_{22}\text{H}_{24}\text{N}_8\text{S}_2\text{AsCl}$: C, 34.30; H, 3.11; N, 14.55; Pt, 25.34;

Found (%) : C, 34.31; H, 3.12; N, 14.56; Pt, 25.40;

Sl. No. 9 : $[\text{PtH}(\text{As}\phi_3)_2(\text{tTH})_2].\text{HSO}_4$: White (M. Pt. >220°C)

Calculated (%) for $\text{PtC}_{22}\text{H}_{25}\text{N}_8\text{S}_3\text{O}_4\text{As}$: C, 31.76; H, 3.00; N, 13.47; Pt, 23.46;

Found (%) : C, 31.67; H, 3.01; N, 13.46; Pt, 23.50;

Results and Discussion

All hydridophosphine and hydridoarsine complexes were diamagnetic indicating d^6 (Ru^{II}) and d^8 (Pt^{II}) configuration in strong ligand field. Analytical results were satisfactory and possible composition is presented in experimental section. All were air stable, monomeric, non-hygroscopic and high melting solids. Molar conductance value in DMF (10^{-3} M) was in agreement with required by a uni-univalent electrolyte for Pt(II) and non-electrolyte nature for Ru (II) complexes. The reflectance spectra of Pt (II) complexes exhibited band in 27700–24490 cm^{-1} region assignable to $^1A_{1g} \rightarrow ^1B_{1g}$ transition in square planar crystal field¹⁵. The other ligand field bands are obscured by CT band observed at 47100–47115 cm^{-1} and it seems to be high degree of $d - p$ mixing in the complexes.

The two spin allowed transitions $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ were observed at 14000–20415 cm^{-1} and 16840–18720 cm^{-1} respectively in Ru(II) complexes indicating octahedral structure¹⁶. A weak spin forbidden transition $^1A_{1g} \rightarrow ^3T_{1g}$ (15125 cm^{-1}) was also observed. The absorption bands around 28450–28570 cm^{-1} of high intensity due to $T_{2g} \rightarrow \pi^*$ transition was located. The octahedral structure of all Ruthenium (II) complexes was assumed considering previous literature.¹⁶⁻¹⁷

IR spectra :

Considering thioamide function of ligand and complexes (table 1) and nature of

shift of thioamide bands of ligand is consistent with thioamide-sulphur coordination.¹⁸⁻²⁰ Thioamide band IV is mainly due to $\nu_C \cdots S$ red shift to lower frequency on complexation indicating bonding through thione sulphur of ligand. Further evidence in support of the coordination of sulphur is provided by new Pt–S and Ru–S stretching vibrations observed at 340 cm^{-1} and 370 cm^{-1} in far IR spectra of complexes respectively. The bonding through imino nitrogen atom was ruled out considering blue shift of thioamide band I and ν_{NH} of ligand on coordination.

All hydridophosphine complexes of Ruthenium (II) display bands at 2060–2085 cm^{-1} and 740–765 cm^{-1} assigned to ν_{Ru-H} and δ_{Ru-H} modes respectively.²¹ A medium band at 1890–1930 cm^{-1} corresponding to $\nu_{C=O}$ mode of coordinated carbonyl group²² and non-ligand bands at 1580(m), 1160(m), 1120(m), 1110(m), 990(m) and 900(s) cm^{-1} due to coordinated $P\phi_3$ molecule was observed. All ionic Platinum (II) hydrides show bands of medium intensity between 2180–2210 cm^{-1} assigned to ν_{Pt-H} and another less intense one between 805–815 cm^{-1} due to δ_{Pt-H} mode²². These assignments are in good agreement with criteria given by Chatt *et al.*²³ with trans effect of $P\phi_3$. Church and Co-workers²⁴ and our previous observations²⁵⁻²⁶ support hydrido ligand and $P\phi_3$ are at trans in square planar structure.

The absorption associated with anions in the complexes are identified at 3420 (m), 1250 (m), 1050 (m) and 1020 cm^{-1} for bisulphate²⁷

and at 1095 (s), 615 and 615(m) cm^{-1} for perchlorate²⁸ and all these correspond to their uncoordinated nature.

NMR spectra :

The ligand (tTH) exhibit a weak signal at δ 3.18 PPM due to thiol hydrogen was not observed in the spectra of complexes indicating bonding through sulphur of thione tautomeric form. The imino proton of ligand observed at 7.7 – 7.72 PPM remain almost unchanged on coordination indicating intact imino proton. All

complexes showed broad signals in the δ 8.2–8.89 PPM range due to aromatic proton of $\text{P}\phi_3$ or $\text{As}\phi_3$.²⁹

The ^{31}P NMR spectrum of $[\text{RuH}(\text{CO})(\text{P}\phi_3)_2(\text{tTH})\text{Cl}]$ was recorded in order to confirm the presence of $\text{P}\phi_3$ groups and to determine the geometry of complex/ The appearance of a signal at 27.48 confirmed the presence of magnetically equivalent phosphorous atom and thus suggesting that the two $\text{P}\phi_3$ groups are mutually trans disposed to each other.³⁰ The

Table 1. Major IR Spectral Bands of the ligand and complexes (cm^{-1})

Compounds	Thioamide Bands				$\nu_{\text{M-H}}/$ (δMH)	$\nu_{\text{C=O}}$	$\nu_{\text{M-S}}/$ ($\nu_{\text{M-P}}$)	Anions Vibr.
	I	II	III	IV				
tTH (ligand)	1550(m)	1297(m) 1250(m)	1055(s)	840(m)	— (-)	—	— (-)	(—)
Ru (II) (SL. No. 1)	1560(m)	1285(m) 1260(m)	1020(m)	800(m)	2060(m) (740m)	1890(m)	370w (485m)	—
Ru (II) (SL. No. 2)	1565(m)	1280(m) 1265(m)	1010(m)	790(m)	2085(m) 745(m)	1910(m)	355w (485m)	—
Ru (II) (SL. No. 3)	1570(m)	1305(m) 1270(m)	1025(m)	805(m)	2105(m) (740m)	1920(m)	335w (475m)	—
Ru (II) (SL. No. 4)	1585(m)	1290(s) 1260(m)	1015(m)	800(m)	2085(m) 785(m)	1930(m)	365w (—)	—
Pt (II) (SL. No. 5)	1565(m)	1280(m) 1255(m)	1010(m)	805(w)	2190(m) (815m)	—	340w (430m)	—
Pt (II) (SL. No. 6)	1570(m)	1285(m) 1265(m)	1020(m)	810(m)	2180(m) (815m)	—	345w (440m)	3420m 1250m 1050m 1020m
Pt (II) (SL. No. 7)	1565(m)	1290(m) 1270(m)	1020(m)	810(m)	2185(m) (810m)	—	345w (420m)	1095m 615m
Pt (II) (SL. No. 8)	1570(s)	1290(s) 275(s)	1010(m)	805(m)	2190(m) (805m)	—	335w (410m)	—
Pt (II) (SL. No. 9)	1585(s)	1285(s) 1270(s)	1005(m)	800(m)	2210(m) (810m)	—	330w (410m)	3425m 1265m 1050m 1025m

Table 2. UV-vis (cm^{-1}) and ^1H NMR (PPM) spectra of ligands and complexes

Compounds	Electronic Spectral Bands (cm^{-1}) (Assignment)	^1H NMR Spectra (PPM)		
		Thiol Proton	Imino Proton	Phenyl Proton
tTH (ligand)	37735 ($\pi \rightarrow \pi^*$) 33115 ($\eta \rightarrow \pi^*$)	3.04	7.6	—
Ru (II) Complex (SL. No. 1)	20415 ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$) 18720 ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$) 15125 ($^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$) 28570 ($\text{T}_{2g} \rightarrow \pi^*$) 34480 (CT, intra ligand)	—	7.65	8.52-7.18
Ru (II) Complex (SL. No. 2)	14000 ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$) 17700 ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$) 13125 ($^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$) 28740 ($\text{T}_{2g} \rightarrow \pi^*$) 35720 (CT, intra ligand)	—	7.60	8.78
Ru (II) Complex (SL. No. 3)	19275 ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$) 16840 ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$) 28400 ($\text{T}_{2g} \rightarrow \pi^*$) 35190 (CT, intra ligand)	—	7.65	8.88
Ru (II) Complex (SL. No. 4)	19450 ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$) 16840 ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$) 28450 ($\text{T}_{2g} \rightarrow \pi^*$) 35190 (CT, intra ligand)	—	7.66	8.11
Pt (II) Complex (SL. No. 5)	27700 ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) 47100 (CT Band)	—	7.65	8.48
Pt (II) Complex (SL. No. 8)	24490 ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) 47115 (CT Band)	—	7.68	8.62

^{31}P nuclei exhibit a downfield shift as compared with those in free ligand. The deshielding may be caused by relatively less donation of electron density from the Ru(II) centre to phosphorous through back bonding, suggesting that the degree of $d\pi - P\pi$ back bonding influences the chemical shift of the phosphorous atoms.

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