

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF RHODIUM (I) COMPLEXES WITH MIXED TRIPHENYLPHOSPHINE AND HETEROCYCLIC THIOAMIDE LIGAND

R.N. Pandey* and A.K.Nag

P.G. Centre of Chemistry(M.U.), College of Commerce, Patna-800020. (India).

*E-mail: rameshwarnath.pandey@yahoo.com

ABSTRACT

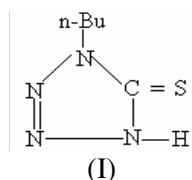
Synthesis and spectral Characterization of a series of mixed –ligand rhodium (I) complexes with triphenyl phosphine and 1-butyl-tetrazoline-5-thione of the type $[Rh(P\phi_3)(CO)(ligand)X]$ ($X= Cl, Br$), $[Rh(P\phi_3)_2(ligand)X]$ ($X=Cl, Br, I, NCS$ and $SnCl_3$) and $[Rh X(P\phi_3)_2(Py)(ligand)]X$ ($X= BF_4$ and PF_6) are reported. The complexes were characterized on the basis of elemental analyses, molar conductance, magnetic susceptibility data, UV-Vis, IR, 1H NMR and ^{31}P NMR spectral studies. A square planar configuration has been tentatively proposed for all these complexes.

Key words: Mixed-ligand, Rh(I) complexes, thioamide ligand.

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INTRODUCTION

Tertiary phosphine complexes of rhodium(I) are versatile catalyst for hydrogenation¹⁻² and hydroformylation³⁻⁶ reactions. Several rhodium(I) complexes with sterically demanding phosphine⁷ have been reported. Osborn et al⁸ and Oro and coworkers⁹ investigated a series of comparable complexes with substituted triphenylphosphine. However, very little attention have been paid to carry out a systematic study on the mixed-ligand phosphine complexes with bulky heterocyclic thioamide. This concomitant paper comprises a resurgence of our interest in the synthesis and spectral characterization of rhodium(I) complexes with mixed-ligand triphenylphosphine and 1-butyltetrazoline-5-thione(I) using wilkinson catalyst² and its analogues as precursors.



EXPERIMENTAL

All chemicals used were either of Anal R or Chemically pure grade. The ligand¹⁰, 1-butyl tetrazoline-5-thione (But5TH) and precursor complexes $[RhX(P\phi_3)_3]^2$ ($X= Cl, Br, I, NCS$), $[Rh(SnCl_3)(P\phi_3)_3]$ ¹¹ $[Rh X(CO)(P\phi_3)_2]^2$ ($X= Cl, Br$), $[Rh(NCS)(CO)(P\phi_3)_2]$ ¹² were prepared by the methods reported in literature.

Preparation of $[Rh(P\phi_3)_2(P_4)(But5TH)]X$; ($X= BF_4, PF_6$)

A solution of $[Rh Cl(P\phi_3)(But5TH)_2]$ (500mg, 0.910m mol) in methanol(25mL) was stirred until the solid dissolved completely and it was then treated with an excess of pyridine (7.58 m mol) in methanol (10mL) for 1 hr. to afford an orange solution. A solution of NH_4BF_4 or NH_4PF_6 (1m mol) in methanol (5mL) was added. The solution was concentrated to half of original volume and 10 mL dry ether was added. Orange coloured solid separated which after filtration was washed with methanol, ether and dried in a vacuum. Yield 85%.

1. C ₄₆ H ₄₅ N ₅ F ₆ SP ₃ Rh	Calculated(%): C 54.70, H 4.45, N 6.93, Rh 10.2 Found(%): C 54.79, H 4.55, N 7.11, Rh 10.2
2. C ₄₆ H ₄₅ N ₅ BF ₄ P ₂ S Rh	Calculated(%): C 58.04, H 4.83, N 7.36, Rh 10.83 Found(%): C 58.12, H 4.95, N 7.56, Rh 10.85

Preparation of [Rh X(Pφ₃)₂ (But5TH)] (X= Cl, Br, I, NCS, SnCl₃)

These complexes were prepared by adopting the similar process as reported by us in the literature¹³.

1. C ₄₁ H ₄₀ N ₄ P ₂ S Cl Rh(Deep Brown)	Calculated(%): C 59.96, H 4.87, N 6.82, Rh 8.07 Found(%): C 60.11, H 4.89, N 6.92, Rh 8.12
2. C ₄₁ H ₄₀ N ₄ P ₂ S Br Rh(Brown)	Calculated(%): C 56.87, H 4.62, N 6.47, Rh 11.90 Found(%): C 57.11, H 4.66, N 6.55, Rh 12.01
3. C ₄₁ H ₄₀ N ₄ P ₂ S I Rh(Brownish Red)	Calculated(%): C 53.94, H 4.49, N 6.14, Rh 11.29 Found(%): C 54.01, H 5.10, N 6.23, Rh 11.30
4. C ₄₂ H ₄₁ N ₅ BF ₄ P ₂ S ₂ Rh(Bright Yellow)	Calculated(%): C 59.71, H 4.97, N 8.29, Rh 12.20 Found(%): C 60.11, H 4.98, N 8.35, Rh 12.31
5. C ₄₁ H ₄₀ N ₄ P ₂ SCL ₃ SnRh(Redish Brown)	Calculated(%): C 48.70, H 4.05, N 5.54, Rh 10.19 Found(%): C 48.92, H 4.10, N 5.64, Rh 10.25

Preparation of [Rh X(Pφ₃) (CO)(But5TH)] (X= Cl, Br)

The suspension of freshly prepared precursor complexes of [Rh X(CO)(Pφ₃)₂](X= Cl, Br) or [Rh(NCS)(CO)(Pφ₃)₂] in benzene and ethanolic solution of 1-butyl tetrazoline-5-thione were taken in 1:1 molar ratio and stirred on magnetic stirrer at 85^oC for two hrs. The working mixture was concentrated to ~ 10mL and 5mL, ether was added to the cold solution as a result a solid matter separated out. It was washed with ether and dried over anhydrous CaCl₂.

1. C ₂₄ H ₂₅ N ₄ O Cl P Rh(Yellow)	Calculated(%): C 49.10, H 4.26, N 9.54, Rh 17.56 Found(%): C 49.16, H 4.28, N 9.68, Rh 17.75
2. C ₂₄ H ₂₅ N ₄ OS P Br Rh(Brown)	Calculated(%): C 45.64, H 3.96, N 8.87, Rh 16.32 Found(%): C 45.92, H 3.98, N 8.82, Rh 16.50
3. C ₂₅ H ₂₅ N ₅ OS ₂ PRh(Brownish Yellow)	Calculated(%): C 49.26, H 4.10, N 11.49, Rh 16.91 Found(%): C 50.10, H 4.11, N 11.50, Rh 17.01

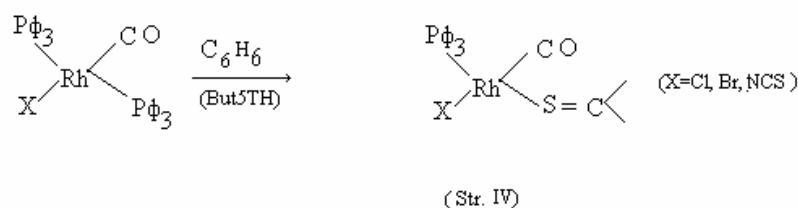
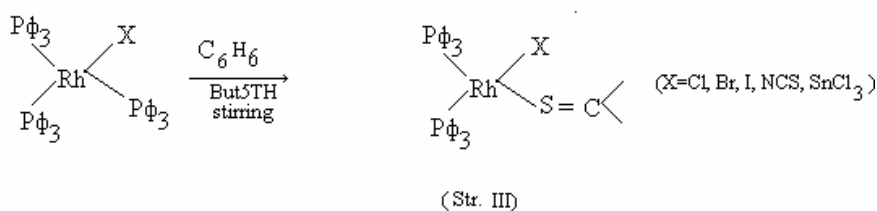
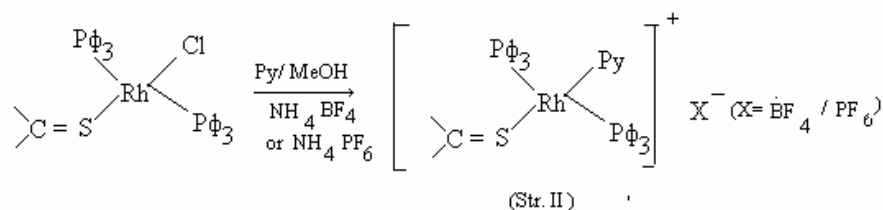
Elemental analysis were performed by the micro- analytical section of the Regional Sophisticated Instrumentation centre, Central Drug Research Institute, Lucknow. IR spectra of ligand and complexes were recorded on a Perkin – Elmer 577 spectrophotometer in the range of 4000-200 cm⁻¹ as KBr pellets and electronic spectra on a Beckmann DU-6, Spectrophotometer. The ¹H NMR and ³¹P NMR spectra were recorded on Bruker 400 MHz or Varian FX 90 Q instruments using TMS and ortho phosphoric acid as references respectively. The magnetic measurements were made on a Gouy balance using Hg[Co(SCN)₄] as calibrant. The molar conductance of complexes (10⁻³M) were measured in DMF using Wiss-Wekstatter Weithem obb Type LBR conductivity meter.

RESULTS AND DISCUSSION

The addition of pyridine to methanol solution of [Rh Cl (Pφ₃)₂(But5TH)] followed by metathetical reaction with NH₄BF₄/ NH₄ PF₆ yielded the corresponding derivatives [Rh(Pφ₃)₂ (Py)(But5TH)]X (X= BF₄/ PF₆) (Str. II).

The other mononuclear precursors display ligand substitution reaction without change in oxidation state of metal leading to the formation of neutral complexes(Str.III and Str. IV). These isolated products are

non hygroscopic, stable, solid and soluble in DMF, DMSO and other coordinating solvents. All complexes were diamagnetic indicating univalent rhodium (Rh^+). However, oxidation state of metal in complexes were verified by the titrating the complexes with ceric ammonium sulphate using ferroin as indicator¹³. The complexes were titrated for two electron charge.



Electronic spectra of complexes display a very broad band of strong intensity between 24680-24000 cm^{-1} assigned to charge transfer band ($T_{2g} \rightarrow \pi^*$). The other ligand field bands are obscured due to strong reducing character of Rh^+ species. These observations are in agreement with our previous work¹⁴⁻¹⁶ observed for thioamide ligands. However, electronic spectrum of $[RhCl(P\phi_3)_2(But5TH)]$ exhibit three bands at 13825, 18320 and 23700 cm^{-1} . The first band(13825 cm^{-1}) is broad and weak while those at 18320 cm^{-1} and 23700 cm^{-1} are medium intensity bands. The first band may be due to spin forbidden $^1A_{1g} \rightarrow ^3A_{2g}$ transition. The other band at 18320 cm^{-1} may be due to spin allowed $^1A_{1g} \rightarrow ^1B_{1g}$ transition. The ligand (But5TH) absorbs around 23700 cm^{-1} , so this band could not be assigned. Thus, rhodium(I) complexes are iso-structural with precursors and are four- coordinated square planar¹⁷.

The ligand (But5TH) contains thioamide group and give rise to four characteristic thioamide bands I($\delta_{NH} + \nu_{C-N}$), II ($\delta_{CH} + \nu_{C-S} + \nu_{C-N}$), III ($\nu_{C-N} + \nu_{C-S}$), IV(ν_{C-S}) in infrared spectra in the region 1500-805 cm^{-1} . Considering normal coordinate analysis (NCA) of thioamides¹⁸, strong Rh-S bond is indicated in all complexes. Thioamide band IV of free ligand red shift to 30-40 cm^{-1} on complexation suggesting bonding through thiocarbonyl sulphur¹⁹⁻²². The bonding through imino nitrogen was ruled out considering blue shift($\sim 15cm^{-1}$) of thioamide band I and ν_{NH} (3055 cm^{-1}) of ligand. Bonding through sulphur is further supported by the presence of new bands at 345 cm^{-1} ($\nu_{asy} Rh-S$), 335 cm^{-1} ($\nu_{sym} Rh-S$) and at 385-390 cm^{-1} (ν_{Rh-P}) in far IR spectra of complexes. Moreover, the presence of single Rh-P stretching mode indicate two $P\phi_3$ group at trans-disposition in square planar structure. All the characteristic bands of $P\phi_3$, CO(carbonyl) and pyridine have been observed in the spectra of complexes²³⁻²⁵.

The characteristic bands due to counter anions were observed at ca. 1100 cm^{-1} for BF_4^- and at 1070 cm^{-1} for PF_6^- in the IR spectra of the respective complexes²⁶. However, the presence of coordinated anions are

confirmed at $2110\text{cm}^{-1}(\nu_{\text{CN}})$, $830\text{cm}^{-1}(\nu_{\text{CS}})$, $482\text{cm}^{-1}(\delta_{\text{NCS}})$ for terminal NCS group²⁷ and at 455cm^{-1} and 4435cm^{-1} for SnCl_3 group²¹.

¹H NMR and ³¹P NMR Spectra

The metal-ligand bonding is further substantiated by ¹H NMR and ³¹P NMR spectra (ii and iii). The complexes (ii and iii) display signals in the δ 8.12-8.89 ppm range due to aromatic protons of $\text{P}\phi_3$ ²⁸. The signal for methyl protons appear as singlet in the range of δ 1.92-2.2 ppm for butyl group. The two middle CH_2 signals are complex and are centred at δ 2.1 and δ 2.3 ppm. The CH_2 group attached to the nitrogen atom of the tetrazoline ring is deshielded giving a triplet at δ 4.72 ppm. The signal due to imino proton is always difficult to identify because of the quadrupole moment of nitrogen and exchange of this proton. However, a peak observed at δ 3.26 ppm in the ligand remains almost at the same position in complexes and imino proton is intact on complexation. The protons of coordinated pyridine²⁶ are observed at δ 7.42, 8.10, 8.68 ppm.

The ³¹P NMR spectra of $[\text{RhCl}(\text{P}\phi_3)_2(\text{But5TH})]$ was recorded in order to confirm the presence of $\text{P}\phi_3$ group and to determine the geometry of the complex. The appearance of a signal around 23.75- 28.78 in the spectrum of complex confirmed the presence of magnetically equivalent phosphorus atoms and suggesting that the two $\text{P}\phi_3$ groups are trans to each other²⁹. The

³¹P NMR spectrum of the complex $[\text{Rh}(\text{P}\phi_3)(\text{P}_y)(\text{But5TH})_2]\text{PF}_6$ consisted of singlet δ 37.56 ppm corresponding to coordinated phosphine ³¹P nuclei. A downfield shift as compared with those in the free $\text{P}\phi_3$ indicate deshielding caused by relatively less donation of electron density from the rhodium(I) centre to phosphorus through back bonding and the high degree of $d\pi - p\pi$ back bonding influences the chemical shift to the phosphorous atom. The ³¹P nuclei of the counter ion PF_6^- resonated at $\delta \sim 103$ ppm in complex in to septet pattern. Thus, ¹H NMR and ³¹P NMR spectral observations are consistent with the conclusions drawn from IR spectral studies.

Table-1: characterization Bands(cm^{-1}) of the IR spectra of rhodium(I) complexes.

Complex	Thioamide Bands(cm^{-1})				$\nu_{\text{Rh-P}}$	$\nu_{\text{Rh-S}}$
	I	II	III	IV		
Ligand (But5TH)	1500(s)	1280(m)	1065(m)	805(m)	-	-
$[\text{Rh}(\text{P}\phi_3)_2(\text{P}_4)(\text{But5TH})]\text{BF}_4$	1515(m)	1270(m)	1050(m)	775(m)	385(m)	345w 385w
$[\text{Rh}(\text{P}\phi_3)_2(\text{P}_4)(\text{But5TH})]\text{PF}_6$	1510(m)	1665(m)	1060(m)	770(m)	390(m)	340w 380w
$[\text{Rh}(\text{P}\phi_3)_2(\text{But5TH})\text{Cl}]$	1505(s)	1270(m)	1065(m)	765(m)	380(m)	345w 390w
$[\text{Rh}(\text{P}\phi_3)_2(\text{But5TH})\text{Br}]$	1510(s)	1272(m)	1062(m)	770(m)	390(m)	340w 385w
$[\text{Rh}(\text{P}\phi_3)_2(\text{But5TH})\text{I}]$	1515(m)	1270(m)	1060(m)	775(m)	385(m)	345w 385w
$[\text{Rh}(\text{P}\phi_3)_2(\text{But5TH})\text{NCS}]$	1510(m)	1265(m)	1065(m)	770(m)	385(m)	340w 390w
$[\text{Rh}(\text{P}\phi_3)_2(\text{But5TH})(\text{SnCl}_3)]$	1504(s)	1270(m)	1070(m)	775(m)	382(m)	345w 385w
$[\text{Rh}(\text{P}\phi_3)(\text{CO})(\text{But5TH})\text{Cl}]$	1505(s)	1275(m)	1075(m)	770(m)	380(m)	340w 390w
$[\text{Rh}(\text{P}\phi_3)(\text{CO})(\text{But5TH})\text{Br}]$	1505(s)	1270(m)	1070(m)	775(s)	385(m)	340w 395w

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