

Mixed-ligand organometallic derivatives of palladium (0), platinum (0) rhodium (1) and iridium (1) with triphenyl phosphine and 1-benzyl-tetrazoline-5-thione

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ABSTRACT

Four coordinate tetrahedral (Pd^0 and Pt^0) and square planar (Rh^+ and Ir^+) complexes of triphenyl phosphine and 1-benzyl tetrazoline-5-thione have been prepared and characterised on the basis of elemental analysis and spectroscopic data (IR, UV-vis, ^1H NMR). Bonding of tetrazole ligand occurs through thione tautomeric form. Determination of oxidation state of central metal atom in the complexes is verified by iodometric and acidimetric titration.

Key words: Pd^0 , Pt^0 , Rh^+ and Ir^+ complexes, Heterocyclic thioamide ligand, structure and bonding.

INTRODUCTION

Organometallic derivatives of Pt-group metals are versatile homogeneous catalyst¹⁻³. They have unique and very interesting insights into structure, bonding and reactivity of molecules in solution. They undergo either coordinative addition or oxidative addition and various stereo-chemical change in solution. We have reported this aspect of study in our previous communications⁴⁻⁸. The present communication describes synthesis, spectral characterization and reactivity study on some new monomeric organometallic derivatives of Pd(0) Pt(0), Rh(1) and Ir(1) with mixed ligand triphenyl phosphine and 1-benzyl-tetrazoline-5-thione (I).

EXPERIMENTAL

All the chemicals used were AR grade 1-benzyl tetrazoline-5-thione was prepared by the

method described by Lieber et al⁹. The precursor complexes $[\text{Pd}(\text{P}\phi_3)_4]^{10}$, $[\text{Pt}(\text{P}\phi_3)_4]^{11}$, $[\text{Rh}(\text{P}\phi_3)_3\text{Cl}]^{12}$, and $[\text{Ir}(\text{Co})(\text{P}\phi_3)_2]^{13}$ were prepared by the methods reported in literature. Benzene solution of these complexes were used in an appropriate molar ratio with ethanolic solution of ligand as reported in our earlier methods¹⁴. The analytical results of complexes are given in Table 1.

Determination of zero oxidation state of central metal atom (Pd^0 and Pt^0) in the complex was verified by iodometric and acidimetric titration reported in literature¹⁵. However, univalent oxidation state of Rh^+ and Ir^+ was found by titrating the complex with ceric ammonium sulphate using ferroin as indicator. The method used was described in the literature¹⁶. All the complexes were titrated for a two-electron change.

IR spectra of ligand and complexes were recorded with Perkin Elmer model 577

spectrophotometer in the range of 4000-200 cm^{-1} as KBr pellets. The electronic spectra were recorded with Zesis (Jena) model of automatic recording system. ^1H NMR spectra of ligand and complexes were recorded with 90 MHz NMR spectrophotometer in CDCl_3 solution using TMS as the internal indicator in the range of 0 to 10 PPM. Molar conductance of complexes were measured in DMF using Wiss-Werkstatter Weithein obb type LBR conductivity meter.

The molecular weight of compounds were measured cryoscopically using highly purified benzene as solvent. Magnetic measurements were made on a Gouy balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant.

RESULTS AND DISCUSSION

All $\{\text{M}(\text{P}\phi_3)_4\}^{17-18}$ [$\text{M}=\text{Pd}/\text{Pt}$], $[\text{Rh}(\text{p}\phi_3)_3\text{Cl}]^{19}$ and $[\text{Ir}(\text{CO})(\text{P}\phi_3)_2\text{Cl}]^{20}$ dissociate in solution and interest with thione tautomeric form of the ligand and the isolated products are given table 1.

Magnetic moment all the complexes were found to be diamagnetic suggesting d^{10} -configuration of the Pd^0 , Pt^0 and d^8 -configuration of Rh^+ and Ir^+ . The suspension of complexes were treated with iodine solution in CCl_4 , the violet colour of iodine was discharge in all cases indicating the presence of Pd^0 , Pt^0 , Rh^+ and Ir^+ electronic state. The zero valent oxidation state of palladium and platinum was verified by iodometric and acidimetric titration. It was found that 1g-mol of $[\text{M}(\text{P}\phi_3)_2(\text{ligand})_2]$ reacts with 2g-equivalent of I_2 and the liberated 2g-mol of ligand consume 2g-equivalent of NaOH , suggesting zero oxidation state of Pt and Pd in complexes¹⁵. The oxidation stat of rhodium and iridium in complexes was found by titration with ceric ammonium sulphate using ferroin as indicator¹⁶. Solutions of all complexes (10^{-3}M) in DMF were non-conducting and molecular weight determination in benzene suggested their monomeric nature. Thus, the known preferential tetrahedral structure for Pd and Pt^0 and square-planar structure for the Rh^+ and Ir^+ complexes was assumed⁵⁻⁷.

Electronic spectra

Electronic spectra of Pd^0 and Pt^0

Table 1: Physico - chemical data of complexes

S. No.	Complex/(Colour)	Analysis % Found/calculated				Thioamide Band IV	λ_{Max} (nm) (Assignments)	Established structure
		C	H	N	M			
1.	$[\text{Pd}(\text{P}\phi_3)_2(\text{BT5TH})_2]$ Yellow	62.0 (61.5)	4.4 (4.5)	10.9 (11.0)	10.5 (10.4)	770 (m)	340 (CT Band)	Td
2.	$[\text{Pt}(\text{P}\phi_3)_2(\text{BT5TH})_2]$ Yellow	56.3 (56.5)	4.2 (4.1)	10.3 (10.1)	18.1 (17.9)	760 (m)	330 (CT Band)	Td
3.	$[\text{Rh}(\text{P}\phi_3)(\text{BT5TH})_2\text{Cl}]$ Brown	51.9 (52.0)	4.0 (3.9)	14.3 (14.2)	13.2 (13.1)	750 (m)	725 ($^1\text{A}_{1g} \rightarrow ^3\text{A}_{2g}$) 550 ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$)	Sq. planar
4.	$[\text{Ir}(\text{CO})(\text{P}\phi_3)(\text{BT5TH})\text{Cl}]$ (Dull Yellow)	45.7 (45.6)	3.1 (3.0)	8.1 (7.9)	27.2 (27.0)	755 (m)	424 (CT Band) ($^1\text{A}_{1g} \rightarrow ^3\text{B}_{1g}$) 350 CT Band	Sq. planar

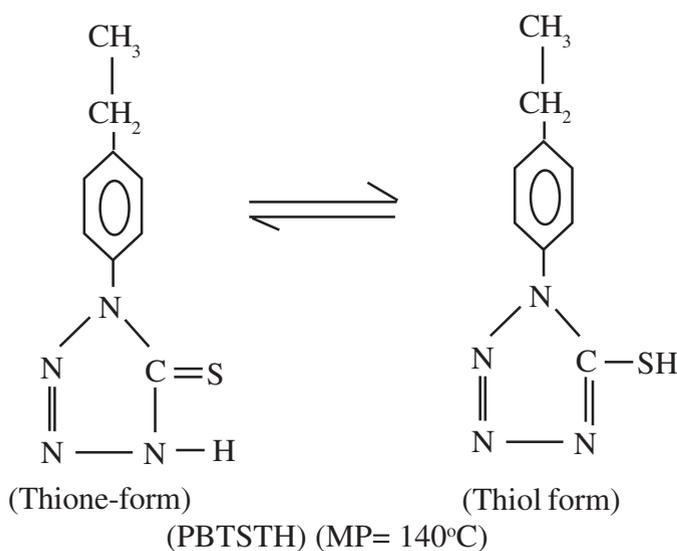
complexes display very strong band of considerable high intensity at 350nm and at 340 nm respectively. The other ligand field bands are obscured by CT band and probably high degree of d-p mixing occurs.

The diamagnetic value of Rh(1) complex suggests the metal ion is in the singlet ground state ($^1A_{1g}$) for coordination number four. The reflectance spectra show three absorption bands at 13793 cm^{-1} (725nm), 18182 cm^{-1} (550 nm) and 23585 cm^{-1} (424 nm) with relative absorption 1:9:10. The band at 13793 cm^{-1} is broad and very weak while those at 18182 cm^{-1} and 23585 cm^{-1} are medium intensity bands. The spectra in pyridine solution show no band at 13793 cm^{-1} and the band at 18225 cm^{-1} appears as shoulder. The disappearance of ligand band at 13793 cm^{-1} may be due to the low solubility of the complex in pyridine and the low extinction coefficient of the transition. The band at 23585 cm^{-1} is also masked by a strong absorption of the pyridine in this region. Thus, the band at 13793 cm^{-1} is tentatively assigned to the spin-forbidden transition $^1A_{1g} \rightarrow ^3A_{2g}$. The band at 18182 cm^{-1} may be due to either spin-forbidden $^1A_{1g} \rightarrow ^3B_{1g}$ transition or the spin-allowed transition $^1A_{1g} \rightarrow ^1B_{1g}$. But higher value of the extinction coefficient (~ 150) suggest it to be the singlet-singlet transition. Thus, the complex $[\text{Rh}(\text{P}\phi_3)(\text{BT5TH})_2\text{Cl}]$ is isostructural with precursor complex $[\text{Rh}(\text{P}\phi_3)_3\text{Cl}]$ and square planar structure may be suggested²¹⁻²².

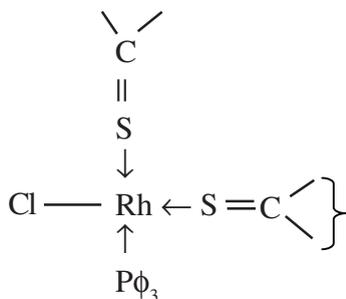
The electronic spectra of $[\text{Ir}(\text{CO})(\text{P}\phi_3)(\text{BT5TH})\text{Cl}]$ display a single very strong band of considerable high intensity at 2857 cm^{-1} and may be assigned to CT band. The other ligand field bands are obscured by CT band probably due to high degree of d-p mixing⁵. So, no positive contribution is obtained in assigning the structure from electronic spectra.

Infrared Spectra

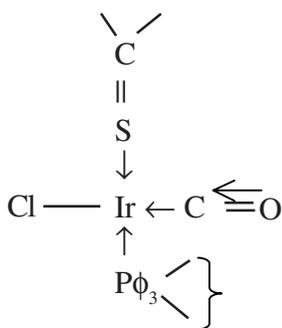
The IR spectrum of ligand (BT5TH) exhibits two distinct broad band of medium intensity in the range $3080\text{-}3020\text{ cm}^{-1}$ are assigned to mixed C-H and N-H stretching vibration²⁴. These bands remain present in the spectra of all complexes almost at the same position and with undiminished intensity indicating absence of bonding through imino nitrogen and N-H hydrogen is intact. The absence of any band in the region 2550 cm^{-1} and 2000 cm^{-1} in the spectra of ligand and complexes (Pd^0 , Pt^0 and $\text{Rh}(1)$) suggest the absence of S-H and Metal-H bonds in the ligand and the complexes respectively. However, weak absorption bands near 1580 , 1435 , 1075 , 1035 and 695 cm^{-1} in the complexes suggest the presence of coordinated $\text{P}\phi_3$ group²⁵ and no such bands are present in the spectrum of BT5TH.



(Fig.1)



Sq. Planar str. of Rh(1) complex
(Fig.II)



Sq. Planar str. of Ir(1) complex
(Fig.III)

The ligand (BT5TH) contains a thioamide group and gives characteristics four thioamide bands²⁶⁻²⁸ at 1510cm⁻¹ (Band I), 1290 cm⁻¹ (Band II) 1050cm⁻¹ (Band III) and at 810cm⁻¹ (Band IV). Thioamide band III and IV have main contributions²⁹ from ν_{C-S} and shifted to lower wave number by about 30-40 cm⁻¹ and 40-60 cm⁻¹ respectively in all complexes indicate the bonding of BT5TH through thione tautomeric sulphur atom and formation of M-S bond in each case was assumed³⁰.

A medium band at 2050 cm⁻¹ in the spectrum of [Ir(CO)(Pφ₃)(BT5TRH)Cl] assigned to $\nu_{C=O}$ mode³¹ which is further supported by new bands at 510(m) and 470(m)cm⁻¹ assigned to ν_{Ir-C} mode³¹. The low position of $\nu_{C=O}$ band is probably due to trans influence of Pφ₃ group.

Metal-ligand vibrations

Far infrared spectra of complexes display

some new bands. Two bands (430 and 410cm⁻¹) and one band at 360cm⁻¹ assigned to ν_{Pd-P} and ν_{Pd-S} modes and two ν_{Pt-S} (340 and 325 cm⁻¹) and one ν_{Pt-P} (425 cm⁻¹) indicate C_{3v}-point group in tetra hedral structure⁵.

The new broad shoulder at 380cm⁻¹, doublet at 355(m)cm⁻¹ and 325(m)cm⁻¹ and a shoulder at 290cm⁻¹ may be assigned to Rh-P, Rh-S and Rh-Cl stretching modes of Rh(1)-complexes. Since, only one ν_{Rh-P} , two ν_{Rh-S} and one ν_{Rh-Cl} bands are observed, the two BT5TH molecules are at cis-position and the chloride atom is trans to one of BT5TH molecules in square planar structure (Fig. II) of [Rh(Pf)(BT5TH)₂Cl]. The lower position of ν_{Rh-Cl} may be due to strong trans influence of thioamide ligands (BT5TH).

The ν_{Ir-P} , ν_{Ir-S} , and one ν_{Ir-Cl} in [Ir(CO)(Pφ₃)(BT5TH)Cl] are observed at 330 cm⁻¹, 295 cm⁻¹ and 225 cm⁻¹ respectively. The low position of ν_{Ir-Cl} suggest chlorine is at Trans position of CO ligands (Fig. III) and the complexes is iso-structural with its precursor Vaska compound.

¹H NMR spectra

All complexes are high soluble in CDCl₃ and ¹H NMR spectra were recorded in this solvent. In Rh(1) and Ir(1) complexes proton signals of the coordinated Pφ₃ is observed in the range of δ 7.2 ppm. Its integral indicates the presence of 15 protons. Hence one Pφ₃ molecule is linked to the RH(1) / or Ir(1) ion through phosphorus atom in square planar complexes³².

The spectra of all complexes display broad multiplet in the δ 7.3 – 7.8 region due to phenyl protons present in BT5TH molecule. The broadening of this peak probably either due to presence of four nitrogen atoms which may cause large quadruple resonance broadening effect or due to ligand exchange reaction occurring in the solution³³. Similar broadening of the phenyl proton signals has been reported by Greaves *et al.*,³⁴. Absorption at δ =2.4 PPM in the spectra of complexes assigned to the CH₃ protons of the ligand. The N-H proton of the ligand is masked by phenyl protons. However, the relative area of phenyl protons signal indicates the presence of imino group. So, amino proton is intact on complexation to Pd⁰, Pt⁰, Rh¹ and Ir¹.

Thus, on the basis of aforesaid observations tetrahedral structure to Pd⁰ and Pt⁰ complexes and square planar structure to Rh¹ and Ir¹ complexes may be tentatively assigned.

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