



SYNTHESIS, CHARACTERIZATION AND REACTIVITY STUDIES ON PHOSPHINE AND ARSINE COMPLEXES OF PALLADIUM (0) LIGATED BY THIOAMIDE LIGAND

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ABSTRACT

Palladium complexes with the formula $[\text{Pd}(\text{As}\phi_3)_2(\text{QTH})_2]$ and $[\text{Pd}(\text{PR}_3)_2(\text{QTH})_2]$ ($\text{R} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$; QTH = 2-mercapto quinazoline-4-one) were synthesized and characterized by elemental analysis, molar conductivity, magnetic susceptibility measurements and spectroscopic (IR, UV-vis, ^1H NMR) methods. All complexes were four-coordinated and tetrahedral oxidation state of Palladium was confirmed by iodometric and acidimetric titration.

Key words: Pd(0), Phosphine, Arsine, Thioamide.

INTRODUCTION

Palladium (0) complexes with phosphine ligands are reviewed¹⁻⁵. These complexes are versatile catalyst for the Tsuji-Trost reactions⁶⁻⁸, Stille⁹ and Suzuki¹⁰ cross-coupling reactions and Heck reactions¹¹. They have interesting insights into structure, bonding and reactivity of molecules and we have reported some Palladium (0) complexes ligated with amide and thioamide and other ligands in our earlier report¹²⁻¹⁶. The present communication reports complexes of Palladium (0) with ligand, which contains both thioamide and amide group together.

EXPERIMENTAL

All chemicals used were of AR grade or CP grade. Solvents were distilled and dried before use. The ligand, 2-mercapto-quinazoline-4-one (QTH)¹⁷ and Precursor complexes,

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[Pd(PE₃)₄] (E = C₆H₅-, n-C₄H₉- C₆H₅CH₂-) and [Pd(Asφ₃)₄] were prepared following previous literature.¹⁸ Tribenzyl phosphine (PBz₃) was prepared using a modification of the reported method¹⁹ as ivory coloured crystals. Triphenyl phosphine (Pφ₃) (M. Pt = 80⁰C), triphenyl arsine (Asφ) (M. Pt = 61⁰C) and tributyl phosphine (PBu₃) were commercial products. Their purity was checked spectroscopically. The zero valent oxidation state of Palladium in complexes was determined by iodometric and acidimetric titration described in literature.²⁰

Preparation of new Pd(0) complexes

All the complexes were prepared using a general method. Benzene solution of precursor complexes were mixed in appropriate molar ratio with ethanolic solution of ligand (QTH) as reported in our earlier method¹².

Analysis

- (i) [Pd(Pφ₃)₂(QTH)] (yellow): Calculated (%) for C₅₂H₄₂N₄O₂P₂S₂Pd (986.4) : C = 63.26, H = 4.25; N = 5.67; Pd = 10.78; Found (%) : C = 63.21; H = 4.30; N = 5.66; Pd = 10.88
- (ii) [Pd(Asφ₃)₂(QTH)₂] (Faint yellow): Calculated (%) for C₅₂H₄₂N₄O₂S₂As₂Pd (1072.4) : C = 58.18; H = 3.91; N = 5.22; Pd = 9.92; Found (%) : C = 58.02; H = 4.01; N = 5.20; Pd = 10.10
- (iii) [Pd(PBu₃)₂(QTH)₂] (yellow): Calculated (%) for C₄₀H₆₆N₄O₂P₂S₂Pd (864.4) : C = 55.52; H = 7.63; N = 6.47; Pd = 12.30; Found (%) : C = 55.62; H = 7.70; N = 6.34; Pd = 12.41
- (iv) [Pd(PBz₃)₂(QTH)₂] (yellow): Calculated (%) for C₅₈H₅₄N₄O₂S₂P₂Pd (1068.4) : C = 65.14; H = 5.50; N = 5.24; Pd = 9.95; Found (%) : C = 65.23; H = 5.01; N = 5.34; Pd = 10.01

Carbon, hydrogen and nitrogen analysis were performed by conventional methods and magnetic measurements were made on Gouy balance using Hg[CO(SCN)₄] as calibrant. IR spectra of ligand and complexes were recorded with the help of Perkin Elmer Model 621 in the range of 4000-200 cm⁻¹ using KBr pellets technique. The electronic spectra of the complexes were obtained in DMF solution (10⁻³ M) using a Cary Model 14 recording spectrophotometer. ¹H NMR spectra were recorded on a high resolution Varian HR-100 (cross coil type) NMR spectrometer in CDCl₃ solution. Molar conductance was measured using 10⁻³ M solution in DMF on a Wiss-Werkstätten-Weitheim obb type LBR conductivity meter.

RESULTS AND DISCUSSION

The coordinative reactivity of phosphine complexes of Ni(0), Pd(0) and Pt(0) has been reviewed by Ugo²¹. [Pd(Pφ₃)₄] dissociate in benzene to give planar species Pd(Psφ₃)₃, which is co-ordinatively unsaturated. There is a close analogy between phosphine and arsine complexes of these zero valent complexes. All the freshly prepared zero valent complexes were soluble in benzene and chloroform but less soluble in these solvents after long standing in air. All were found to non-conducting in DMF and diamagnetic nature. The diamagnetic nature suggested d¹⁰-configuration for Pd(0). However, determination of oxidation state of palladium was verified by iodometric and acidimetric titration²⁰. When a suspension of these complexes in CCl₄ were treated with iodine solution in CCl₄, the violet colour of iodine got discharged suggesting zero valent palladium²².

When aqueous solution of HBF₄ is treated with [Pd(Pφ₃)₂(QTH)₂] then yellow solid products was isolated and was found to be uni-bivalent electrolyte.²³



One molecule of hydrogen per mole of Pd was evolved. Excess of triphenyl phosphine did not displace the coordinated water molecule even in refluxing in methanol. Thus, it was assumed that [Pd(Pφ₃)₂(QTH)₂] is formed from [Pd(Pφ₃)₄] without change in oxidation state of metal which further undergoes oxidative addition reaction with HBF₄. The molecular weight of [Pd(Pφ₃)₂(QTH)₂] in highly purified benzene consistent with formulation and suggested monomeric nature of the complex.

Electronic spectrum of [Pd(Pφ₃)₂(QTH)₂] exhibits a single very strong band around 395 nm of considerable high intensity. The other ligand field bands are obscured by charge transfer band and probably high degree of d-p mixing has occurred. The common tetrahedral structure of all complexes was assumed considering previous literature¹².

IR Spectra

A comparison of infrared spectral bands of Pφ₃, Asφ₃, PBu₃, PBz₃, QTH and complexes indicate the following facts :

No absorptions attributable to νPd-H occurred in the spectra of complexes, so it was assumed that Pd(0) compounds can not be hydrides. The metal sensitive new bands at 1435, 1090, 500, 430, 395, 245 and 210 cm⁻¹ (Pφ₃)²⁴, at 1440, 1080, 665, 475, 315 and 240 cm⁻¹ (Asφ₃)²⁵ and at 1115 and 2910 cm⁻¹ (PBu₃)²⁶ in complexes indicated coordinated phosphine

ligands. The characteristic bands of QTH at 3445 (sb), 3350 (s) (νNH), 1710 cm^{-1} (νCO) and 1530 cm^{-1} (thioamide band I) remained practically unaltered on complexation indicating non-coordination of N-H and C=O groups. Thus, absence of bonding through N and O atoms was assumed considering our previous observations²⁷⁻²⁸ and Singh et al.²⁹

However, thioamide band II (1295 cm^{-1}), band III (960 cm^{-1}) and band IV (790 cm^{-1}) red shift to lower frequency (Table 1) on coordination indicating bonding through sulphur of thioamide group which increases CN bond order and decreases CS bond order³⁰⁻³². Two bands at 350-355 and 340-330 ($\nu\text{Pd-S}$) and two bands at 430-425 cm^{-1} and 420-416 cm^{-1} ($\nu\text{Pd-P}$) suggest C_{2v} point group in tetrahedral structure of $[\text{Pd}(\text{PR}_3)(\text{QTH})_2]$ ($\text{R} = \text{C}_6\text{H}_5$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{-}$ and $\text{C}_6\text{H}_5\text{-CH}_2\text{-}$) agreement with previous literature¹⁶.

Table 1: Major IR spectral bands (cm-1) of ligand (QTH) and complexes

Compounds	νNH	Thioamide Bands ^ψ				$\nu\text{Pd-S}$	$\nu\text{Pd-P}$
		Band I	Band II	Band III	Band IV		
QTH (ligand)	3445 (sb) 3350 (s)	1530 (s)	1295 (s)	960 (m)	790 (m)	-	-
$[\text{Ru}(\text{P}\phi_3)_2(\text{QTH})_2]$	3450 (sb) 3365 (sb)	1535 (sb)	1275 (m)	950 m	765 (m)	350 w 340 w	430 m 420 m
$[\text{Ru}(\text{As}\phi_3)_2(\text{QTH})_2]$	3440 (sb) 3355 (sb)	1530 (sb)	1270 (m)	945 m	760 m	355 w 345 w	435 m 425 m
$[\text{Ru}(\text{PBU}_3)_2(\text{QTH})_2]$	3445 (s) 3360 (sb)	1532 (s)	1265 (s)	940 m	765 m	365 w 350 w	440 m 435 m
$[\text{Ru}(\text{PBZ}_3)_2(\text{QTH})_2]$	3450 (s) 3355 (sb)	1535 (sb)	1265 (m)	945 (m)	752 (m)	340 w 340 w	435 w 430 w

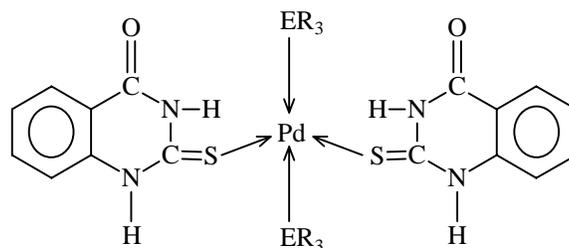
ψ Mixed bands : Band I = $\delta\text{NH} + \delta\text{CH} + \nu\text{C=N}$; Band II = $\nu\text{C=N} + \delta\text{NH} + \delta\text{NH} + \nu\text{C=S}$,
Band III = $\nu\text{C-S} + \nu\text{C-N}$; Band IV = $\nu\text{C-S}$

¹H NMR Spectra

The ¹H NMR of ligand and Pd(0) complexes (Sl. No. 1, 2 & 3) were recorded in CDCl_3/TMS to substantiate metal-ligand bonding. The broad multiplet around $\delta 8.5\text{-}7.0$ PPM ($\text{P}\phi_3$)³³, $\delta 6.2\text{-}7.8$ PPM ($\text{As}\phi_3$)³⁴ and $\delta 7.15\text{-}7.32$ PPM (PBZ_3)³⁵ in phosphine ligands are assigned due to aromatic protons of phenyl ring. The strong signals at $\delta 2.78$ PPM in PBZ_3

are due to methylene (CH₂) protons of benzyl group. The aromatic protons signals of QTH are observed at δ 7.62-7.72 ppm. The aromatic at position -5 in QTH is deshielded by carbonyl oxygen and the extreme signal at δ 8.12 ppm is considered due to this proton. The signal due to N-H groups are observed around δ 3.2 ppm in QTH. These protons are observed almost unchanged in position on complexation indicating non-participation of N-H groups of QTH and no deprotonation during ligand substitution reactions in precursors. Hence, bonding of thioamide ligand occurs only through thiocarbonyl sulphur atom.

Thus, on the basis of aforesaid discussion, tetrahedral structure may be proposed to all Pd(0) complexes (Structure I).



Tetrahedral structure of [Pd(ER₃)₂(QTH)₂]
(E = P/As; R = C₆H₅-, C₆H₅-CH₂-, CH₃CH₂CH₂CH₂-)

(Structure I)

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