

Low-Ligated Complexes of Palladium (O) and their Oxidative reaction products with Inorganic Acids

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Abstract

Low-ligated Palladium (O) complexes of the type $[Pd (P\phi_3)_2 (ligand)_2]$ are synthesized with precursor $[Pd (P\phi_3)_4]$ in benzene by the ligand substitution reaction. All isolated products are stable solid and the palladium atom is tetra coordinated having tetrahedral configuration. The oxidative addition products of precursor and new isolated products with inorganic acids are examined using elemental analysis, infrared, 1H NMR, ^{31}P NMR and electronic spectral data.

Key Words : Palladium (O), Heterocyclic thioamide, oxidative addition.

Introduction

Palladium (O) phosphine complexes are among the most versatile transition metal catalysts used for organic synthesis¹. The metal catalysed hydroformylation, hydrogenation and cross-coupling reactions are reported by various workers²⁻⁵. The present paper is devoted to synthesis, characterization and oxidative addition of inorganic acids to palladium (O) complexes.

Experimental

All chemicals used were of AR grade

or CP grade. The ligand, 1-butyl tetrazoline-5-thione⁶ and precursor complex⁷, $[Pd (P\phi_3)_4]$ were prepared by the method reported in literature. All complexes were prepared by oxidative addition of ethanolic solution of inorganic acid (30%) to $Pd (P\phi_3)_4$. The ligand displacement reaction to $Pd (P\phi_3)_4$ with 1-butyl tetrazoline-5-thione yielded $[Pd (P\phi_3)_2 (ButSTH)_2]$ as reported earlier following our previous method⁸. Oxidative addition with this complex also yielded complexes given in table 1.

Elemental analysis were performed by the micro-analytical section of the Regional

Sophisticated Instrumentation Centre, C.D.R.I. Lucknow. IR spectra of ligand and complexes were recorded on a Perkin-Elmer 577 spectrophotometer in the range of $400\text{-}200\text{ cm}^{-1}$ as KBr pellets and electronic spectra on a Beckmann DV-6, spectrophotometer. The ^1H NMR and ^{31}P NMR spectra were recorded on Bruker 400 MHz or Varian FX 90 Q instruments using TMS and orthophosphoric acid as references respectively. The molar conductance of complexes (10^{-3} M) were measured in DMF using Wiss-Wekstatter Weithem Obb type LBR conductivity meter. The magnetic measurements were made on a Gouy balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. Melting points were recorded with Raaga heating table and uncorrected.

Results and Discussion

All complexes are prepared from precursor agree very well with analytical data. Ligand substitution in benzene with $\text{Pd}(\text{P}\phi_3)_4$ occurs easily and the yield of products are almost quantitative. Oxidative addition to $[\text{Pd}(\text{P}\phi_3)_4]$ and $[\text{Pd}(\text{P}\phi_3)_2(\text{ligand})_2]$ with ethanolic solution of HCl , HNO_3 , H_2SO_4 , HClO_4 and HBF_4 yielded stable solids listed in table 1.

One mol of H_2 (g) per mol. of Palladium was evolved with ethanolic acids. However, when oxidative addition reaction was carried out with aqueous acid then $[\text{Pd}(\text{P}\phi_3)(\text{H}_2\text{O})(\text{ligand})_2]\text{X}_2$ ($\text{X} = \text{Cl}, \text{ClO}_4^-, \text{BF}_4 \& \text{NO}_3$) was isolated. The coordinated water molecule could not be replaced even in refluxing in CH_3OH using excess of $\text{P}\phi_3$. When ligand substitution reaction was carried out in CS_2 or Pyridine followed by addition of ethanolic HCl then

$[\text{Pd}(\text{P}\phi_3)_3(\text{CS})]\text{Cl}_2$ and $[\text{Pd}(\text{P}\phi_3)_3(\text{Py})]\text{Cl}_2$ were yielded.

The molar conductance value in DMF (10^{-3} M) is in agreement with required by a uni-bivalent electrolyte indicating ionic nature of chloride, nitrate and perchlorate. These observations was further supported by chemical analysis of Na_2CO_3 extract of complexes and infrared spectra.

The ligand field bands in the electronic spectra of complexes at $27600\text{-}27700\text{ cm}^{-1}$ ($^1\text{A}_{1g} \rightarrow ^1\text{E}_g$), $23790\text{-}23750\text{ cm}^{-1}$ ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) and at $21600\text{-}21740\text{ cm}^{-1}$ ($^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$) are in agreement with the transition suggested for four coordinated Pd (II) complexes having square planar structure⁹⁻¹¹. The diamagnetic behavior of complexes also supports these observations. The other bands in UV – region assigned to intra-ligand charge transfer.

IR Spectra :

The characteristic bands due to $\nu_{\text{N-H}}$ (3090 cm^{-1}) and thioamide band I (1510 cm^{-1}) of free ligand remain present on coordination indicating absence of bonding through imino nitrogen atom of the ligand. However, thioamide band IV (805 cm^{-1}) of free ligand red shift to lower wave number in order of $35\text{-}40\text{ cm}^{-1}$ on complexation indicating bonding of thioamide ligand through sulphur¹². The formation of metal-sulphur bond is also supported by appearance of a new band at $420\text{-}410\text{ cm}^{-1}$ in far IR spectra of complexes and assigned due to Pd-S stretching mode.¹³ Moreover, the presence of single $\nu_{\text{Pd-S}}$ mode is due to trans-

Table 1. Analytical and Physical Data of Complexes

Sl. No.	Complex/ (Colour, MP, °C)	Analysis % Found/ (Calculated)			Molar Cond. ($\pi^{-1}\text{cm}^2\text{mol}^{-1}$)
		C	H	Pd	
1.	[Pd (P ϕ_3) ₂ Cl ₂] (yellow, 288)	61.80 (61.59)	4.29 (4.27)	15.20 (15.16)	6.8
2.	[Pd (P ϕ_3) ₃ (CS)]Cl ₂ (light brown, 140)	65.85 (65.51)	4.42 (4.46)	10.68 (10.56)	137.23
3.	[Pd (P ϕ_3) ₃ (Py)]Cl ₂ (yellow, 115)	68.11 (67.92)	4.82 (4.79)	10.52 (10.20)	139.46
4.	[Pd (P ϕ_3) ₂ (NO ₃) ₂] (yellow, 170)	57.36 (57.26)	4.01 (3.97)	14.15 (14.10)	6.20
5.	[Pd (P ϕ_3) ₃ (H ₂ O)] (ClO ₄) ₂ (faint yellow, 230)	58.32 (58.40)	4.32 (4.23)	9.63 (9.59)	135.23
6.	[Pd (P ϕ_3) ₂ (SO ₄)] (dull yellow, 155)	59.31 (59.30)	4.01 (4.11)	14.76 (14.60)	3.50
7.	[Pd (P ϕ_3) ₃ (H ₂ O)] (BF ₄) ₂ (light yellow, 210)	59.69 (59.77)	4.44 (4.32)	9.80 (9.82)	130.50
8.	[Pd (P ϕ_3) ₂ (But5TH) ₂] (yellow, 120d)	58.22 (58.32)	5.38 (5.28)	11.32 (11.24)	6.20
9.	[Pd (P ϕ_3) (H ₂ O) (But5TH) ₂] (NO ₃) ₂ (deep yellow, >250)	40.92 (40.67)	3.28 (3.26)	12.98 (12.88)	135.60
10.	[Pd (P ϕ_3) (H ₂ O) (But5TH) ₂] (ClO ₄) ₂ (faint yellow, >280)	37.33 (37.27)	3.01 (2.99)	11.85 (11.80)	125.20

disposition of two thione ligands in square planar configuration. The absorption associated with anions in complexes are identified at 1360 and 810 cm^{-1} for ionic nitrate (Sl. No. 9), at 1515 cm^{-1} ($\nu_{\text{as}}\text{NO}_2$), 1135 cm^{-1} ($\nu_s\text{NO}_2$), 1025 cm^{-1} (ν_{NO}) and 810 cm^{-1} (δNO_2) of coordinated

nitrate group (C_{2v}) (Sl. No. 4), at 1265 cm^{-1} ($\nu_{\text{as}}\text{SO}_2$), 1160 cm^{-1} ($\nu_s\text{SO}_2$), 1105 cm^{-1} ($\nu_{\text{as}}\text{SO}_2$) and 920 cm^{-1} ($\nu_s\text{SO}_2$) for coordinated sulphato group (Sl. No. 6), at 1090 cm^{-1} and 620 cm^{-1} for ionic perchlorate (Sl. No. 5 &

Table 2. IR and Electronic Spectral Data

Compound	IR Spectral Data (cm ⁻¹)				Electronic Spectral Data Bands / (Assignments)
	Thioamide Bands*				
	I	II	III	IV	
(C ₅ H ₁₀ N ₄ S) (ligand)	1510	1280	1065	805	38460 ($\pi\text{-}\pi^*$) 32785 ($n\text{-}\pi^*$)
[Pd (Pφ ₃) ₂ (But5TH) ₂]	1515	1260	1045	765	37740 (Intra ligand CT band)
[Pd (Pφ ₃) ₂ (But5TH) ₂]Cl ₂	1505	1270	1050	770	37720 (CT Band) 27780 (¹ A _{1g} → ¹ E _g) 23800 (¹ A _{1g} → ¹ B _{1g}) 21700 (¹ A _{1g} → ¹ A _{2g})
[Pd (Pφ ₃) (H ₂ O) (But5TH) ₂](BF ₄) ₂	1515	1260	1040	775	38560 (CT Band) 27790 (¹ A _{1g} → ¹ E _g) 23800 (¹ A _{1g} → ¹ B _{1g}) 21690 (¹ A _{1g} → ¹ A _{2g})
[Pd (Pφ ₃) (H ₂ O) (But5TH) ₂](NO ₃) ₂	1525	1255	990	773	37740 (CT Band) 27770 (¹ A _{1g} → ¹ E _g) 23870 (¹ A _{1g} → ¹ B _{1g}) 21670 (¹ A _{1g} → ¹ A _{2g})
[Pd (Pφ ₃) (H ₂ O) (But5TH) ₂](ClO ₄) ₂	1520	1275	980	770	37760 (CT Band) 27790 (¹ A _{1g} → ¹ E _g) 23860 (¹ A _{1g} → ¹ B _{1g}) 21665 (¹ A _{1g} → ¹ A _{2g})

* Mixed Bands, Band I ($\delta_{\text{NH}} + \delta_{\text{CH}} + \delta_{\text{C=H}}$);

Band II ($\nu_{\text{C=S}} + \nu_{\text{C=N}} + \delta_{\text{NH}} + \delta_{\text{CH}}$)

Band III ($\nu_{\text{C=S}} + \nu_{\text{C=N}}$)

Band IV ($\nu_{\text{C=S}}$)

10), at 1060 cm^{-1} for ionic tetrafluoroborate (Sl. No. 7) and at 480 cm^{-1} for coordinated chloride (Sl. No.1). All aqua complexes display new bands at 3410 cm^{-1} ($\nu_{\text{H}_2\text{O}}$), 1605 cm^{-1} ($\delta_{\text{H}_2\text{O}}$), 790 cm^{-1} ($\pi_{\text{H}_2\text{O}}$) and 490 cm^{-1} ($\nu_{\text{Pd-O}}$) indicating the presence of coordinated water molecule in complexes. The systematic shift of thioamide bands of ligand confirm bonding of ligand through thiocarbonyl sulphur considering our earlier observations¹¹⁻¹³. The characteristic bands due to $\text{P}\phi_3$ ¹⁴ and Pyridine¹⁵ were also present in the expected region.

¹H NMR and ³¹P NMR Spectra :

The ligand to metal bonding is further supported by ¹H NMR and ³¹P NMR spectra. All the complexes showed broad signals in the range $\delta 8.23$ - 8.95 PPM range due to aromatic proton of $\text{P}\phi_3$ molecule.¹⁶ The resonances in the region 7.70 , 8.05 and 8.80 PPM assignable to the proton of coordinated Pyridine (Sl. No. 3) along with the resonances due to aromatic protons of $\text{P}\phi_3$. The Pyridine proton resonances exhibited down field as compared to that in free ligand indicate the complexation of Pyridine nitrogen atom with metal centre.¹⁷ All aqua complexes exhibit singlet signal at $\delta 1.32$ PPM corresponding to two protons. The triplet at 1.72 PPM for methyl proton and two middle CH_2 signals are complex and are centred at 2.1 and 2.4 PPM for butyl group of ligand. The CH_2 group attached to nitrogen atom of the tetrazoline ring is deshielded giving a triplet at 4.82 PPM in the complexes (Sl. No. 8, 9 & 10). The peak observed at 3.30 PPM in the ligand (But5TH) remains almost at the same

position in complexes and assigned to N-H proton of coordinated ligand which is intact after complexation.

The ³¹P NMR spectra of two complexes (Sl. No. 1 & 8) were recorded in order to confirm the presence of $\text{P}\phi_3$ groups and to determine the geometry of the complexes. The appearance of a signal around 28.76 PPM in the spectrum of complexes confirmed the presence of magnetically equivalent phosphorous atom and the suggesting that the two $\text{P}\phi_3$ groups are trans to each other.¹⁸ These observations are consistent with the conclusion drawn from electronic and IR Spectra and square planar structure to all Pd (II) and tetrahedral structure to Pd (O) complexes may be tentatively assigned.

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