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METAL DERIVATIVES OF ORGANO-PHOSPHORUS COMPOUND LIGATED BY ORGANIC ACIDS

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ABTRACT

Palladium (0) and Platinum (0) derivatives of triphenyl phosphine ligated by organic acids are prepared and characterized using elemental analysis, magnetic moment, conductometric, IR, UV-vis and ^{1}H NMR spectral data. The unionised and unco-ordinated free-COOH group is present in metal-phosphine derivatives.

Key words: Metal^0-Pϕ_3, Anthranilic acid, Thioacetic acid.

INTRODUCTION

Metal derivatives of tertiary phosphines are versatile catalyst[1-2] used for organic synthesis[3], cross-coupling reactions[4-5], hydrogenation of alkenes[6], hydroformylation reactions[7] and metal precursors[8]. Some low-valent metal derivatives of triphenyl phosphine mixed with thioamides[9], amides[10] and sulphide[11] ligands are reported in our earlier communications. The present study describes reaction of organic acids with metal derivatives of triphenyl phosphine. A thorough investigation on structure and nature bonding in reaction products of organic acids and metal derivatives of triphenyl phosphine are reported herein.

EXPERIMENTAL

All chemicals used were of AR grade and CP grade. The anthranilic acid (AAH), triphenyl phosphine (Pϕ_3) and thioacetic acid (TAH) were obtained from E. Merck. Solvents were dried before use. The palladium (0)[12] and platinum (0)[13] derivatives of triphenyl phosphine were prepared by the methods reported in literature. All solid metal derivatives of M(Pϕ_3)$_4$ (M = Pd/Pt) was ligated by organic acids using a general method:

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The freshly prepared $M(P\phi_3)_4$ (M = Pd/Pt) (1 m mol) in dry benzene (100 cm^3) were mixed with organic acids (2 m mol) and the mixture was stirred on magnetic stirror for 1 hr at 85^oC in a covered beaker. The solution mixture was concentrated and cooled. The solid products obtained were filtered, washed with dry benzene and dried in vacuum desiccator over fused calcium chloride (yield = 70.75%). Carbon, hydrogen and nitrogen analysis were performed by conventional methods and results are reported in Table 1.

IR spectra of ligands and their 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 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 $CDCl_3$ solution. The magnetic measurements were made on a Gouy balance using Hg $[Co(SCN)_4]$ as calibrant.

RESULTS AND DISCUSSION

Benzene solution of $M(P\phi_3)_4$ (M = Pd/Pt) undergoes ligand substitution reaction without change in oxidation state of metals. All isolated solid products are non-electrolyte in DMF (10^{-3}) and found to be diamagnetic as expected for d^{10} complexes (Pd^0 & Pt^0). Electronic spectra of complexes exhibit single vary strong band of very high intensity between 37740-35840 cm^{-1} due to charge transfer. Hence, all isolated products are iso-structural with their precursor compounds and common tetrahedral structure was assumed considering our previous observations[9-11].

IR Spectra

A comparison of IR spectra of organic acids and their ligand substitution products indicate the following :

(i) Appearance of strong bands at 1710-1700 cm^{-1} in free anthranilic acid and its derivatives suggest un-ionised and un-coordinated free –COOH group[14]. The ionised and coordinated carboxylic group exhibits COO stretching bands near 1650-1590 cm^{-1}.[15]

(ii) The ν_{asym} (NH_2) and ν_{sym} (NH_2) in free anthranilic acid are observed at 3400 cm^{-1} and 3300 cm^{-1} red shift to lower frequency by 30-35 cm^{-1} and 40-45 cm^{-1}, respectively, indicating the formation of metal-N bond. This is also corroborated by the presence of new bands in far IR spectra of complexes at 480 cm^{-1} and 360 cm^{-1} (Pd^0) and at 485 cm^{-1} and 380 cm^{-1} (Pt^0) due to metal-N stretching modes.

(iii) Triphenyl phosphine exhibits large number of bands in the low-frequency region[16-17]. The new bands at 215 cm^{-1} and 235 cm^{-1} (Pd^0) and at 225 cm^{-1} and 239 cm^{-1} (Pt^0) tentatively assigned to metal-P stretching mode having some ligand contribution.

(iv) Bands at 1466 cm^{-1} and 1430 cm^{-1} are due to δ CH$_3$ modes of coordinated thioacetic acid molecule in complexes (S. No. 2 & 4).

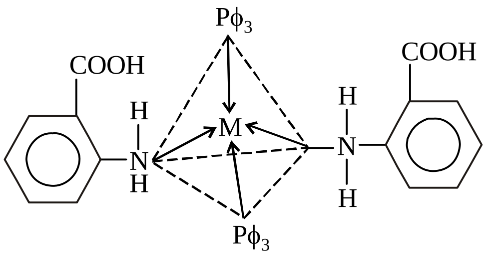
(v) There is a strong band at 760 cm^{-1} in the spectrum of free thioacetic acid shifts to 740 cm^{-1} on coordination to all zero valent metal ion indicating coordination of CH_3CSOH through sulphur. The presence of new weak bands at 368 cm^{-1} and 320 cm^{-1} (Pd^0) and at 420 cm^{-1} and 425 cm^{-1} (Pt^0) in far IR of complexes also supports the formation metal-S bond.

^{1}H NMR Spectra

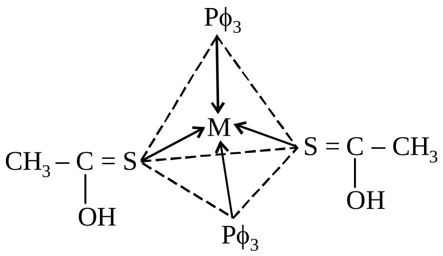
The free anthranilic acid display signals between δ 7.72-6.52 (multiplet), δ 8.4 and at δ 3.6 ppm due to phenyl protons, amino protons and proton of -O-H group, respectively.

The amino protons are low field shifted on complexation and the integrated intensities of the signals agree with assigned structure of complexes. The phenyl protons and OH protons are also slightly low field shifted and the integrated intensities of these signals agree well the formulation of complexes. These protons are intact on coordination and consistent with the results of infrared spectra of complexes. The signals found at δ 8.70-8.10 ppm range as broad multiplet in complexes are due to aromatic protons of coordinated $P\phi_3$ molecules[18].

Thus, on the basis of above observations the tetrahedral structure is tentatively assigned for all four coordinated Pd(0) and Pt(0) complexes.



Tetrahedral structure of $[M(P\phi_3)_2(AAH)_2]$
(M = Pd/Pt)



Tetrahedral structure of $[M(P\phi_3)_2(TAH)_2]$
(M = Pd/Pt)

Table 1: Analytical and physical data of complexes

S. No.	Complex/ (Colour)	M. Pt. (^{0}C)	Analysis (%) : Found/(Calculated)				Molar Cond. (Ohm^{-1} cm^2 mol^{-1})
			C	H	N	Metal	
1.	$[Pd(P\phi_3)_2(AAH)_2]$ (Grey)	141	67.88 (67.84)	5.04 (4.97)	3.49 (3.16)	12.10 (12.03)	12.32
2.	$[Pd(P\phi_3)_2(TAH)_2]$ (Yellow)	146d	61.38 (61.34)	4.88 (4.85)	-	13.60 (13.59)	10.62
3.	$[Pt(P\phi_3)_2(AAH)_2]$ (Grey)	129	61.60 (61.66)	5.01 (4.83)	2.88 (2.87)	20.10 (20.14)	10.83
4.	$[Pt(P\phi_3)_2(TAH)_2]$	138d	55.30 (55.42)	4.38 (4.36)	-	22.41 (22.38)	13.24

d = decomp.

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