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Ligation of Phosphine and Arsine Complexes of Palladium (0) by Secondry Thioamide

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Abstract

Some stable phosphine and arsine complexes of Palladium (0) ligated with ethylene thiourea of composition $[Pd(RE_3)_2(etu)_2]$ ($E = C_6H_5$, $C_6H_5CH_2$& n-C_4H_9; R = P/As) are reported. The compositions of the complexes have been established by elemental analysis, magnetic susceptibility measurements, conductivity, IR and UV-vis spectral data. All complexes are four-coordinated and tetrahedral in which ligand acts as neutral monodentate.

Key words : Pd(0), Thioamide, Tetrahedra.

Introduction

There has been significant and enhancing developments in organometallic chemistry of Palladium (0) owing to their use and application for organic synthesis[1], efficient catalytic system for the cross-coupling reactions[2-4], Tsuji-Trost reactions[5-7], Catalyzed Heck reaction[8-10], borylation of aryl halides[11], isomerisation of alkene[12] and other reactions.[13] The present study aims at synthesis, structure and spectroscopic investigation of some novel Palladium (0) complexes ligated by ethylene thiourea.

Experimental

All chemicals used were of AR grade or CP grade. The ligand ethylene thiourea[14] and precursor Palladium (0) complexes[15] were prepared by the method reported in literature. All new Palladium (0) complexes were prepared by ligand substitution in benzene in precursors $Pd^0(PE_3)_4$ ($E = C_6H_5$, $C_6H_5CH_2$- & n-C_4H_9-) and $Pd(As\phi_3)_4$ following our previous method.[16] Tribenzyl phosphine (PBz_3) was prepared using a modification of the reported method[17] as ivory coloured crystals.

IR Spectra were recorded on a Perkin Elmer 577 spectrophotometer and electronic spectra on a BackMann DU-6 spectrophotometer. Molar conductance of complexes were measured in DMF (10^{-3} M) using Wiss-Werkstatten Weihem obb type LBR conductivity meter. Magnetic measurements were made on a Gouy balance using $Hg(Co(SCN)_4]$ as calibrant.

Results and Discussion

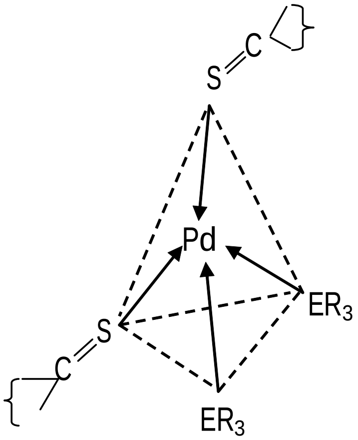
Elemental analysis and molecular weight determination indicated the molecular formula $[Pd(PR_3)_2(ETU)_2]$ (R = C_6H_5-; $C_6H_5CH_2$- and n-C_4H_9-). All isolated products were dismagnetic indicating d^{10}– configuration (Pd^0). Suspension of these complexes discharged the violet colour of iodine in CCl_4 which also supported the zero valent Palladium.[18] The zero valent oxidation state of Palladium was further verified by iodometric and acidimetric titration reported in literature.[19] The molar conductance of complexes were measured in DMF (10^{-3} M) was found in the range of 8.30 – 13.62 π^{-1} cm^2mol^{-1} which indicated their non-electrolytic nature.[20]

Electronic spectra of complexes exhibited a single very broad band around 44248 – 37590 cm^{-1} due to charge transfer and high degree of d-p mixing may be suggested in these complexes.[21]

IR Spectra :

Infrared spectra of ethylenethiourea have been studied by several workers.[22-24] Agarwala and Bhaskara Rao[25] performed normal coordinate analysis (NCA) of ethylenethiourea molecule. A comparison of spectra of ethylenethiourea and corresponding complexes indicates the formation of Pd-S bond through thiocarbonyl sulphur of ligand. The ν_{NH} band of ethylenethiourea present at 3250 cm^{-1} has become split on coordination and the split bands have appeard at 3330 and 3275 cm^{-1} in the spectra of complexes indicating NH group has not been displaced by Pd(0). Thioamide band I (table 1) blue shift on complexation suggesting absence of bonding through imino nitrogen atom and NH proton is intact.

Thioamide band II observed at 1200 cm^{-1} is supported by NCA of ligand split on complexation and observed at 1220 and 1196 cm^{-1} with considerably reduced intensities. This may be due to increase in C=N bond order and very slight decrease in C=S bond order on complexation of ligand through thiocarbonyl sulphur.[26-27] Thioamide band III and Band IV has major contribution from $\nu_{C=S}$ red shift to lower frequencies on complexation confirms coordination through thione sulphur considering our previous observations.[21] New bands at 275 – 280 cm^{-1} and 230 – 242 cm^{-1} in complexes are assigned to $\nu_{Pd\text{-}S}$. New bands at 373 – 342 cm^{-1} and 375 – 335 cm^{-1} in complexes are assigned to Pd-As and Pd-P stretching modes. Thus, normal tetrahedral structure of all new complexes may be proposed considering our earlier observations.[28-30]



Tentative Td – Str.
of $[Pd(ER_3)_2(etu)_2]$ (R = C_6H_5-; $C_6H_5CH_2$- & n-C_4H_9; E = P/As)

Table 1. Analytical and Physical data of Pd (0) Complexes

Complex/ (MF)	Colour	Analysis (%) : Found/(Calcd)				Molar Cond. ($\wedge_m^{-1}cm^2mol^{-1}$)
		Pd	N	C	H	
$[Pd(P\phi_3)_2(ETU)_2]$ $(PdC_{42}H_{42}N_4P_2S_2)$	Yellow	12.68 (12.74)	6.66 (6.70)	60.36 (60.37)	5.13 (5.03)	13.62
$[Pd(P\phi_3)(ETU)_3]$ $(PdC_{27}H_{33}N_6PS_3)$	Greenish Yellow	15.77 (15.76)	12.41 (12.44)	48.10 (48.00)	4.89 (4.88)	8.30
$[Pd(As\phi_3)_2(ETU)_2]$ $(PdC_{42}H_{42}N_4As_2S_2)$	Light Yellow	11.42 (11.53)	6.12 (6.07)	54.32 (54.64)	4.56 (4.55)	14.32
$[Pd(PBu_3)_2(ETU)_2]$ $(PdC_{30}H_{66}N_4P_2S_2)$	Yellow	14.90 (14.88)	7.77 (7.83)	50.40 (50.36)	9.33 (9.23)	12.36
$[Pd(PBz_3)_2(ETU)_2]$ $(PdC_{48}H_{54}N_4P_2S_2)$	Yellow	11.56 (11.58)	6.00 (6.09)	70.48 (70.52)	5.88 (5.87)	13.30

Table 2. Characterization IR Spectral Bands (cm^{-1})

Compound	ν_{NH}	Thioamide Bands ψ				ν_{Pd-P}	ν_{Pd-S}
		Band I	Band II^c	Band III^d	Band IV^f		
ETU (ligand)	3250	1530^a 1505^b	1200	1040^d 919^e	685^f	-	-
$[Pd(P\phi_3)_2(ETU)_2]$	3330 3275	1544 1521 1518	1230 1190	1030,995 905	650	375 335	275 230
$[Pd(P\phi_3)(ETU)_3]$	3325 3280	1535 1510	1225 1198	1025,990 910	656	370 340	282 235
$[Pd(As\phi_3)_2(ETU)_2]$	3330 3280	1540 1520 1518	1220 1190	1020 985 905	650	373 342	280 242
$[Pd(PBu_3)_2(ETU)_2]$	3330 3275	1535 1520 1510	1210 1185	1010 986 907	640	375 330	282 245
$[Pd(PBz_3)_2(ETU)_2]$	3330 3295	1545 1532 1515	1225 1180	1015 990 900	645	370 325	278 240

ψ: Mixed Bands; a = 60% δ_{sym} N-H + 20% ν_{sym} C-N; b = 80% δ_{sym} N-H + 12% ν_{sym} C-N; c = 30% sym C-N + 36% $\nu_{C=S}$; d = 34% ν_{sym} CH_2-N + 34% $\nu_{C=C}$ + 26% + $\nu_{C=S}$; e = 28% νCH_2-N + 24% ν_{C-C} + 19% $\nu_{C=S}$ + 15% ν_{sym} + 15% ν_{sym} C-N; f = 46% ν_{C-N} + 30% ν_{C-S} + 11% sym-ring deformation.

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