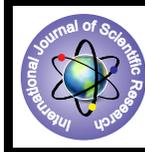


Low-Valent Organometallic Derivatives of Palladium (0), Platinum (0), Rhodium (I) and Iridium (I) with Ammonium Salt of Thioglycolic Acid



CHEMISTRY

KEYWORDS : Td-M0 and Square-planar MI species, Triphenyl phosphine, Structure, Bonding.

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ABSTRACT

Palladium (0), Platinum (0), Rhodium (I) and Iridium (I) derivatives of triphenyl phosphine ligated by ammonium salt of thioglycolic acid are prepared, characterized and structure are deduced using elemental analysis, magnetic moment, conductance, IR, UV-vis and ¹H NMR spectral data. The unionised and uncoordinated free –COONH₄ group is present and bonding occurs through thiol sulphur.

INTRODUCTION

Low-valent organometallic complexes of Pd(0), Pt(0), Rh(I) and Ir(I) with amide¹, thioamide²⁻⁴ and other ligands⁵ are reported in our earlier communications. This concomitant paper comprises a resurgence of our interest in thioglycolic acid which has unique and interesting mode of coordination at different pH range⁶⁻⁸. The precursors used in the present study are Vaska catalyst⁹, [Ir(PPh₃)₂(CO)Cl], Wilkinson catalyst¹⁰, [Rh(PPh₃)₂(CO)Cl], Williamson catalyst, [Pt(PPh₃)₄], and Grubb's catalyst¹¹, [Pd(PPh₃)₄] and their solid reaction products with ammonium salt of thioglycolic acid are isolated and structural elucidation using various physico-chemical and spectral data is reported.

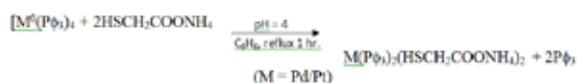
EXPERIMENTAL

All chemicals used in the present work were CP-grade or AR-grade. Thioglycolic Acid (Fluka), triphenyl phosphine (Albright and Wilson Ltd.) and other reagents were commercial product were used as such. All new complexes were prepared by ligand substitution reactions between precursor complexes and ammonium salt of thioglycolic acid in benzene following our previous method.³ Elemental analysis, magnetic measurements, molecular weight determination, conductivity measurements, IR, UV-vis and ¹H NMR spectra were obtained as reported in our previous paper.¹²

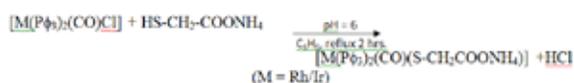
RESULTS AND DISCUSSION

All solid products were isolated by ligand substitution reactions in benzene using precursors and ammonium salt of thioglycolic acid at different pH.

Scheme – I :



Scheme – II :



All solid products isolated after substitution reaction were diamagnetic indicating d¹⁰ configuration for Pd⁰ and Pt⁰ and d⁸ configuration for Rh^I and Ir^I species. The violet colour of iodine solution was discharged by them supporting their respective oxidation state. However, the determination of univalent oxidation state of rhodium in complexes was further verified by using titrating complex with ceric ammonium sulphate using ferroin as indicator¹³ and oxidation state of platinum and palladium was confirmed by iodimetric and acidimetric titration.¹⁴ The elemental analysis of complexes are consistent with proposed formula given in table 1. Molar conductance of complexes (10⁻³ M) in DMF indicate their non-electrolytic nature.¹⁵

Spectral Characterization

IR Spectra :

A comparison of IR spectra thioglycolic acid and their reaction products indicates the following :

- The free thioglycolic acid exhibits ν_{S-H} for sulphahydril group at 2560 cm⁻¹ is not found in the spectra of Rh(I) and Ir(I) complexes implying that mercapto group is ionized and coordinated¹⁶. However, this band is red shifted to lower frequency in Pd(0) and Pt(0) complexes by 30-35 cm⁻¹ indicating coordinated nature of –SH group. These observations are further supported by new bands at 380-385 cm⁻¹ in Pd(0) complexes and at 370-375 cm⁻¹ in Pt(0) complexes due to Metal-S stretching modes.
- The terminal coordinated carbonyl group in Rh(I) and Ir(I) complexes are observed at 2010 cm⁻¹ and 2050 cm⁻¹ respectively consistent with previous literature.¹⁷ Such bands are not observed in other Pd(0) and Pt(0) complexes.
- The strong vibrations at 535, 690, 760 and 1550 cm⁻¹ in complexes confirmed the coordinated PPh₃ molecules¹⁸. The new non-ligand bands around 440-450 cm⁻¹ due to Metal-P stretching mode supports the coordinated PPh₃ molecules in complexes. Triphenyl phosphine (PPh₃) exhibits large number of bands in low-frequency region¹⁹, so some contributions of these bands may not be ruled out.
- The presence of coordinated Pyridine²⁰ is indicated by broad band in the region of 3500-3400 cm⁻¹ and medium to weak intensity bands at 670, 455 and 250 cm⁻¹ in the spectrum of [Pd(PPh₃)₂(Py)(HS-CH₂COONH₄)]. Such bands are not observed in the spectra of other complexes and HSCH₂COONH₄.

UV-vis Spectra :

The electronic spectra of zero valent palladium and platinum complexes display a very broad and strong band between 28555 - 33400 cm⁻¹ of considerable high intensity due to charge transfer. The other ligand field bands are obscured by CT band and high degree of d-p mixing was assumed considering previous observations and the known preferential tetrahedral structure of all Pd(0) and Pt(0) complexes tentatively proposed¹⁴. The very strong band between 25000-28600 cm⁻¹ in rhodium (I) complex is assigned due to charged transfer band from filled metal 4d² orbital empty ligand π*-orbital and square planar Rh(I) may be assumed considering previous literature.²¹

¹H NMR Spectra

The metal-ligand bonding is further substantiated by ¹H NMR. The complexes display signals in the 8.31-7.34 PPM range due to coordinated PPh₃ molecules.²² The thiol proton of thioglycolic acid observed at 8.28 PPM was found to be absent in Rh(I) and Ir(I) complexes indicating deprotonation of –SH group during complexation. However, multiplet in the range of 8.05-1.25 PPM in Pd(0) and in the range of 8.163-1.22 PPM in Pt(0) com-

plexes confirms the presence of –SH group and coordination through thiol sulphur atom.

Thus, on the basis of aforesaid discussion tetrahedral structure to four coordinated Pd(0) and Pt(0) and square planar structure to four coordinated Rh(I) and Ir(I) complexes may be proposed.

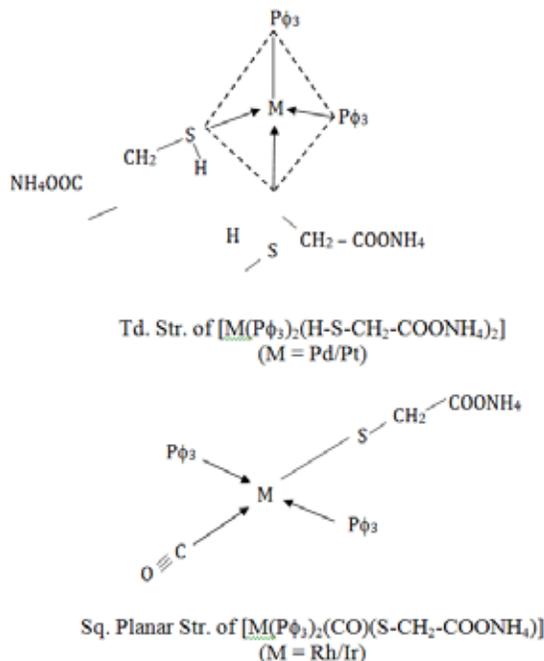


Table 1 : Analytical and Physical data of complexes

Complex/ (MF)	pH of isola- tion	Colour/ (M. Pt)	Analysis % Found/(Calcd)				λ_m ($\text{\AA}^{\circ}\text{cm}^{-2}\text{mol}^{-1}$)
			C	H	N	Metal	
$[Pd^0(P\phi_3)_2(HS-CH_2COONH_4)_2]$ ($PdC_{40}H_{44}O_4N_2P_2S_2$)	4	Brown (138 d)	56.66 (56.57)	5.24 (5.18)	3.18 (3.30)	12.12 (12.54)	10.30
$[Pt^0(P\phi_3)_2(HSCH_2COONH_4)_2]$ ($PtC_{40}H_{44}O_4N_2P_2S_2$)	4	Golden brown (220 d)	51.10 (51.22)	4.70 (4.69)	3.01 (2.98)	20.75 (20.81)	8.32
$[Pt^0(P\phi_3)_2(HSCH_2COONH_4)]$ ($PtC_{36}H_{32}O_3NSP_2$)	4	Pale rose (110)	61.66 (61.65)	4.21 (4.12)	1.21 (1.28)	17.80 (17.88)	8.60
$[Pd^0(P\phi_3)_2(Py)(H-SCH_2-COONH_4)]$ ($PdC_{43}H_{42}O_2N_2P_2S$)	6	Moon- stone (210)	63.12 (63.04)	5.22 (5.13)	3.44 (3.42)	12.98 (13.00)	10.12

$[Rh^I(P\phi_3)_2(CO)(S-CH_2COONH_4)]$ ($RhC_{34}H_{36}O_3NSP_2$)	6	Brown (215 d)	61.30 (61.33)	4.73 (4.71)	2.00 (1.83)	13.50 (13.49)	10.16
$[Ir^I(P\phi_3)_2(CO)(SCH_2COONH_4)]$ ($IrC_{39}H_{36}O_3NSP_2$)	6	Yellow brown (225 d)	55.01 (54.92)	4.30 (4.22)	1.66 (1.64)	22.62 (22.53)	10.12

Table 2 : IR (cm⁻¹), ¹H NMR (δ PPM) and UV-vis (nm) spectral data of ligand and complexes

Compound	IR (cm ⁻¹)			¹ H NMR (δ PPM)			λ_{max} (nm)
	vSH	vM-S	vM-P	CH ₂ Proton	SH Proton	P ϕ_3 Proton	
LH ^ψ	2665	-	-	3.35	2.18	-	
$[Pd^0(P\phi_3)_2(LH)_2]$	2640	380	445	3.73 – 3.49 (multi- plet)	2.15 – 2.04 (multi- plet)	8.34 – 7.28	28555
$[Pd^0(P\phi_3)_2(Py)(LH)]$	2630	378	440	3.71 – 3.49 (multi- plet)	1.62 – 1.25 (multi- plet)	8.34 – 7.34	33400
$[Pt^0(P\phi_3)_2(LH)_2]$	2645	385	450	3.77 – 3.31 (multi- plet)	1.63 – 1.25 (multi- plet)	7.63 – 6.93	33460
$[Pt^0(P\phi_3)_2(LH)]$	2635	388	455	4.25 – 3.71 (multi- plet)	1.61 – 1.22 (multi- plet)	8.31 – 7.22	33300
$[Rh^I(P\phi_3)_2(CO)(L)]$	-	388	445	3.54 – 3.08 (multi- plet)	-	8.35 – 7.32	25000
$[Ir^I(P\phi_3)_2(CO)L]$	-	380	440	3.62 – 3.48 (multi- plet)	-	8.33 – 7.33	28600

$\Psi = LH = HS - CH_2 - COONH_4$

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