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Organometallic Derivatives of Rhodium (1) Ligated with Heterocyclic Thioamides

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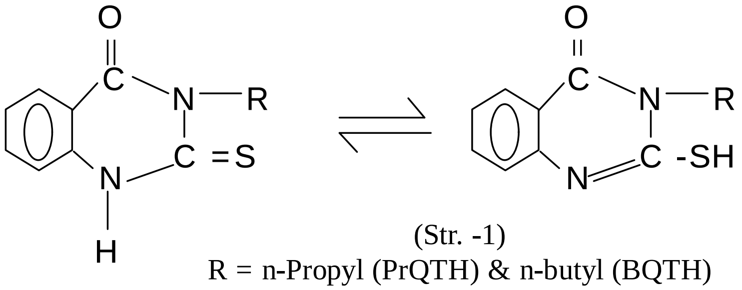
Abstract

Mixed ligand organometallic complexes of Rhodium(1) with triphenyl phosphine and n-propyl and n-butyl derivatives of 2-mercapto-3-alkyl-quinazoline-4-one have been prepared and characterized by elemental analysis, conductometric, magnetic, IR UV-vis and ‘H NMR spectral data. All Thodium(1) complexes are iso-structural with precursor. The thioamide ligands acts as neutral monodentate having bonding through thione tautomeric form.

Key words : Rh(1), Thioamide, phosphine square planar.

Introduction

Organometallic complexes of Rhodium(1) are versatile catalyst[1-3] for many organic reactions and subject of reviewed[4-6]. They have interesting insight into structure, bonding and reactivity of molecules which either undergo coordinative addition or dissociation in solution[7]. The concomitant paper comprises a resurgence of our interest in the synthesis and spectral characterization of Rhodium(1) complexes with mixed ligand triphenyl phosphine and 2 mercapto- 3- alkyl- quinazole- 4- one(I) using Wilkinson catalyst[8] as precursor.



(Str. -1)
R = n-Propyl (PrQTH) & n-butyl (BQTH)

Experimental

All chemicals used were CP grade or AR grade. Solvents were distilled and dried before use. The ligands[8] and precursor complex[3], $[Rh(P\phi_3)_3Cl]$were prepared by the methods reported in literature.

Preparation of complexes :

Preparation of $[Rh(P\phi_3)_2(Py)(ligand)]^+X^-$; (X= BF_4, PF_6)

These complexes were prepared following our previous method reported in literature[9].

Sl. No. 1: $[Rh(P\phi_3)_2(Py)(PrQTH)]BF_4$ (Light orange):

Calculated (%) for $RhC_{52}H_{47}N_3OP_2SBF_4$ (1012.81) :
C = 61.61; H = 4.61; N = 4.14; Rh = 10.15;
Found (%) : C = 61.71; H = 4.70; N = 4.10; Rh = 10.20

Sl. No. 2 : $[Rh(P\phi_3)(Py)(PrQTH)]PF_6$(Light orange):

Calculated (%) for $RhC_{52}H_{47}N_3OP_3SF_6$ (1070.87) :
C = 58.27; H = 4.38; N = 3.92; Rh = 9.60;
Found (%) : C = 58.30; H = 4.40; N = 4.00; Rh = 9.62

Sl. No. 3 :$[Rh(P\phi_3)_2(Py)(BQTH)]BF_4$ (Orange):

Calculated (%) for $RhC_{53}H_{49}N_3OP_2SBF_4$ (1026.71) :
C = 61.94; H = 4.77; N = 4.09; Rh = 10.02;
Found (%) : C = 62.03; H = 4.78; N = 4.00; Rh = 10.10

Sl. No. 4: $[Rh(P\phi_3)(Py)(BQTH)]PF_6$ (Orange):

Calculated (%) for $RhC_{53}H_{49}N_3P_3SF_6$ (1084.87) :
C = 58.62; H = 4.51; N = 3.87; Rh = 9.48;
Found (%) : C = 58.65; H = 60; N = 3.88; Rh = 9.50

Preparation of $[RhCl(P\phi_3)(CO)(ligand)]$:

A suspension of $RhCl(P\phi_3)_3$(0.5 g) in C_6H_6 (15 ml), 2-mercapto-3-alkyl-quinazoline-4-one (1 m mol in 20 ml MeOH) and benzaldehyde (1 ml) were stirred on magnetic stirrer at 85° C for two hrs. The solution rapidly turned pale yellow was concentrated to ~15 ml and ether was to cold solution and solid compounds separated out. It was filtered washed with ether and dried over anhydrous $CaCl_2$.

Sl. No. 5 : $[RhCl(P\phi_3)(CO)(PrQTH)]$ (yellow):

Calculated (%) for $RhC_{30}H_{27}O_2N_2PSCl$ (648.4) :
C = 55.52; H = 4.16; N = 4.32; Rh =15.86;
Found (%) : C = 55.55; H = 4.21; N = 4.33; Rh = 15.88

Sl. No. 6: $[RhCl(P\phi_3)(CO)(BQTH)]$ (brownish yellow):

Calculated (%) for $RhC_{31}H_{27}N_2O_2PSCl$ (662.4) :
C = 56.16; H = 4.07; N = 4.22; Rh =15.53;
Found (%) : C = 56.22; H = 4.11; N = 4.32; Rh = 15.55

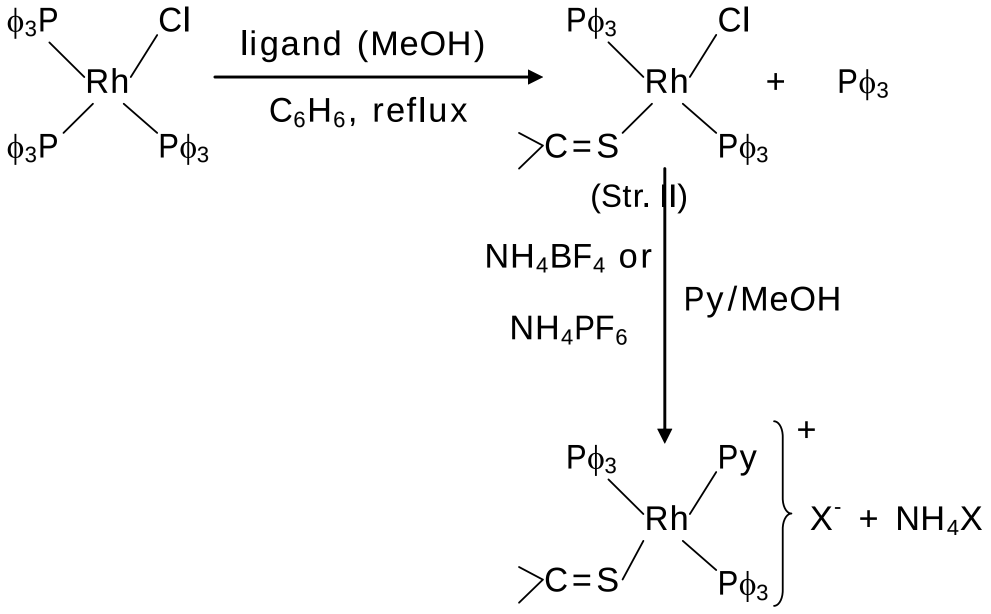
Elemental analysis were performed at the micro-analytical section of the Regional Sophisticated instrumental centre, CDRI, Lucknow. IR spectra of ligands and complexes were recorded on a perkin-Elmer 577 spectrophotometer in the range of 4000-200 cm^{-1} as

KBr pellets and Electronic spectra on a Beckmann DU-6, spectrophotometer. The ‘HNMR spectra were recorded on Bruker 400 MHz instruments using TMS as reference. The magnetic measurements were made on a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant. The molar conductance of complexes (10^{-3} M) were measured in DMF using Wiss-Wekstatter Weitheim obb type LBR conductivity meter.

Results and Discussion

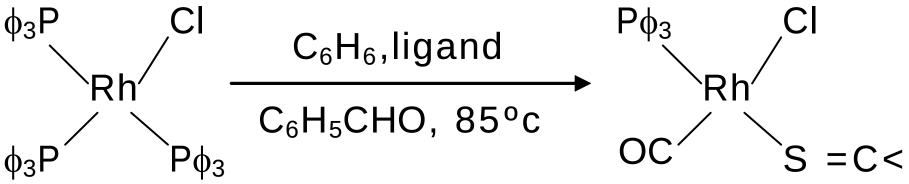
The ligands PrQTH or BQTH display ligand substitution reaction to yield $[RhCl(P\phi_3)_2(ligand)]$. The addition of Pyridine to methanol solution of $[RhCl(P\phi_3)_2(ligand)]$ followed by metathetical reaction with NH_4BF_4/ NH_4PF_6 yielded the corresponding derivatives $[Rh(P\phi_3)_2(Py)(ligand)]^+X^-$ (X = BF_4/ PF_6; ligand = PrQTH/ BQTH)

Scheme – I :



(Str. III) (X = BF_4/ PF_6)

Scheme – II :



Str. (IV)

All isolated products were nonhygroscopic, stable solid and soluble in DMF, DMSO and other coordinating solvents. All were non conducing in DMF(10^{-3} M) but molar conductance of $[Rh(P\phi_3)_2(Py)(ligand)]^+X^-$; (X = BF_4, PF_6) were found in the range of 30-40$\wedge^{-1}$ cm^2 mol^{-1} indicating their electrolytic nature and consistent with previous literature[10]. All complexes were diamagnetic indicating univalent rhodium (Rh^+). However, oxidation state of metal in complexes was confirmed by titrating the complexes with ceric ammonium sulphate using ferroin as indicator[11]. The complexes were titrated for two electron charge.

Electronic spectra of complexes display a very broad band of strong intensity between 24740-24000 cm^{-1} assigned to charge transfer band ($T_2g \rightarrow \pi^*$). The other ligand field bands are obscured probably due to strong reducing character of Rh^+ species. These observations are in agreement with our previous work[12-14] observed for thioamide ligands. However, electronic spectrum of $[RhCl(P\phi_3)_2$ (ligand)] exhibit three bands at 13840 cm^{-1} ($^1A_1g \rightarrow {}^3A_2g$), 18425 cm^{-1} ($^1A_1g \rightarrow {}^1B_1g$) and at 23400$cm^{-1}$. The band at 23400 cm^{-1} could not be assigned because the ligands also absorb in this region.

Thus, all Rhodium(1) complexes are iso-structural with precursors and are four-coordinated square planar[15].

IR Spectra :

The characteristic IR bands observed in the spectra of ligands at 3225-3200cm^{-1} (νNH), 1680cm^{-1} (νCO) and 1530-1525cm^{-1} (thioamide band I) remained practically unaltered on complexation indicating non-coordination of imino nitrogen and carbonyl oxygen atom. However, thioamide band III (1030-995cm^{-1}) and thioamide band IV (800 cm^{-1}) red shift to lower freque ncy by 30-40cm^{-1} and 35-45cm^{-1} respectively indicating bonding through thiocarbonyl sulphur atom[16-18]. New bands at 320-315cm^{-1} in complexes supports the formation of Rh-S bond and are assigned to stretching modes. A single non-ligand band at 410cm^{-1} in $[Rh(CO)(P\phi_3)_2(Py)]^+X^-$ (X = BF_4/PF_6) indicates the trans disposition of two $P\phi_3$ groups in square planar structure.

The non-ligand bands at 2080-2035cm^{-1} in complexes assigned to νCO of terminally coordinated carbonyl group which is observed at higher frequency than in precursor complex. It appears that CO absorption move to lower frequencies as the ligand size increases.

New bands at 470-480cm^{-1} in complexes are assigned to νRh-Cl and the absorption associated with anions in complexes are identified at 1105cm^{-1} for BF_4 and 1070 cm^{-1} for PF_6 in the spectra of corresponding complexes[19]. The Pyridine ring vibrations in the higher frequency region are not shifted appreciably but in-plane-deformation (604cm^{-1}) and out-of-plane ring deformation (405cm^{-1}) shifted to higher frequency on complexation[20]. The $P\phi_3$ vibrations are also observed as our previous report[21]. Thus, both ligands acts as neutral monodentate having coordination through thione sulphur atom in square planar structure.

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Table 1. Major IR(cm^{-1}) spectral Bands of ligands and complexes.

Compounds	νNH	νC=O	Thioamide Bands ψ				νRh-Cl	νRh-S
			Band I	Band III	Band III	Band IV		
PrQTH	3200	1680	1530	1285	1030	800	-	-
Sl. No. 1	3230	1685	1535	1290	1005	780	470	315
Sl. No. 2	3210	1682	1540	1290	990	770	480	320
Sl. No. 5	3215	1690	1535	1295	985	775	475	325
BQTH	3225	1685	1525	1300	995	805	-	-
Sl. No. 3	3230	1690	1530	1310	980	740	480	325
Sl. No. 4	3235	1686	1535	1315	970	745	475	330
Sl. No. 6	3240	1695	1527	1310	925	760	485	325

ψ = Band I = δNH + νC=N);
Band II = ν C=S + δC=N + δCH);
Band III =νC=N + νC ⋯ S); Band IV=νC ⋯ S)

Table 2. 'H NMR (PPM) spectral data of ligands and Rh(1)complexes

Compds.	Aromatic Protons	CH_3 Protons	CH_2 Protons	CH_2-N Protons	Pyridine Protons			$P\phi_3$ Protons
					α	β	γ	
PrQTH	7.6 8.3	1.75	2.2	4.7	-	-	-	-
Sl. No. 1	7.8 8.4	1.74	2.23	4.8	7.62	8.18	8.78	8.12
Sl. No. 2	7.7 8.3	1.75	2.24	4.8	7.7	8.2	8.8	8.23
Sl. No. 5	7.8 8.5	1.77	2.25	4.7	-	-	-	8.78
BQTH	7.78 8.3	1.8	2.23	5.4	-	-	-	-
Sl. No. 3	7.82 8.5	1.76	2.12.2	4.8	7.76	8.1	8.8	8.21
Sl. No. 4	7.7 8.4	1.78	2.22.3	4.8	7.7	8.2	8.7	8.32
Sl. No. 6	7.6 8.3	1.73	2.42.1	4.8	-	-	-	8.60

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^{1}*H NMR spectra:*

'H NMR spectra of ligands and complexes were recorded in $CDCl_3$/TMS to substantiate further metal-ligand bonding. The aromatic protons signals are observed at δ7.8-8.5 PPM and the aromatic proton at position-5 is deshielded by carbonyl oxygen and observed at δ8.3 PPM. The methyl proton of butyl group are observed as triplet at δ1.73 PPM and the two middle CH_2 signals are complex and are centred at δ2.1 and δ2.3 PPM. The CH_2 group attached to nitrogen atom of the quinazole ring is deshielded giving a triplet at δ4.8 PPM. The n-propyl proton signals at δ1.76 (t, CH_3), δ2.2 (CH_2) and δ4.7 PPM for CH_2 attached to nitrogen atom. The imino proton signals in free ligand are observed almost unchanged in position at δ3.2 PPM on complexation indicating NH proton is intact. The aromatic protons of $P\phi_3$ ligand resonated as broad multiplet in the range δ7.52-7.18 PPM in complexes.

The resonances in the region δ7.60, δ8.18 and δ8.90 PPM assignable to the protons of coordinated Pyridine along with the resonances due to aromatic protons in Pyridino complexes. The Pyridine proton resonances exhibited down field as compared to that in free Pyridine. These observations are consistent with conclusions drawn from IR spectral data.

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