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Mixed-Ligand Complexes of Palladium (II), Ruthenium (II), Rhodium (III) and Iridium (III) with Triphenyl Phosphine and Dibenzyl Sulphide

R.N. PANDEY* and KALPANA SHAHI

P. G. Centre of Chemistry (M.U), College of Commerce, Patna - 800 020 (India).
E-mail: rameshwarnath.pandey@yahoo.com

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ABSTRACT

The synthesis and characterization of mixed-ligand Pd(II), Ru(II), Rh(III) and Ir(III) complexes with triphenyl phosphine and dibenzyl sulphide are reported. The complexes have been characterized by analytical, conductance, magnetic susceptibility, IR, electronic, ^1H NMR and ^{31}P NMR spectral data. Palladium (II) complex is four-coordinated square planar and other ruthenium (II), rhodium (III) and iridium (III) are six-coordinated octahedral.

Key words: Pt-metals, Complexes triphenyl phosphine, Dibenzyl sulphide.

INTRODUCTION

Mixed-ligand phosphine complexes of late transition metals are versatile homogeneous catalyst and subject of review.¹⁻⁶ A variety of catalytic processes involve metal precursors modified with triphenyl phosphine, plays a major role.⁷⁻⁸ The present communication reports synthesis, characterization and structural investigations of some new Pd (II), Ru (II), Rh (III) and Ir (III) complexes of triphenyl phosphine and Dibenzyl sulphide. Prior to this work, James et al⁹ have reported Trichlorotris (dibenzyl sulphide) rhodium (III) as effective catalyst for the hydrogenation of maleic acid and trans-cinnamic acid.

EXPERIMENTAL

All chemicals used were of CP-grade or AR-grade. Solvents were distilled and dried before use. The ligand dibenzyl sulphide (R_2S)¹⁰ and the precursor complexes $[\text{Pd}(\text{PPh}_3)_2(\text{R}_2\text{S})_2]$ ¹¹, $[\text{RuH}(\text{CO})(\text{PPh}_3)_3\text{Cl}]$ ¹², $[\text{Ru}(\text{PPh}_3)_4\text{Cl}_2]$ ¹³, $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ ¹⁴, and $[\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}]$ ¹⁵ were prepared by the methods reported in literature. The Pd(II) complex was prepared by oxidative addition between precursor complex and 30% ethanolic solution of HCl . The preparation of ruthenium (II) complexes were similar to our earlier method.¹⁶ The Rh (III) and Ir (III) complexes were prepared by ligand substitution reactions in benzene with precursors complexes followed by the oxidative-

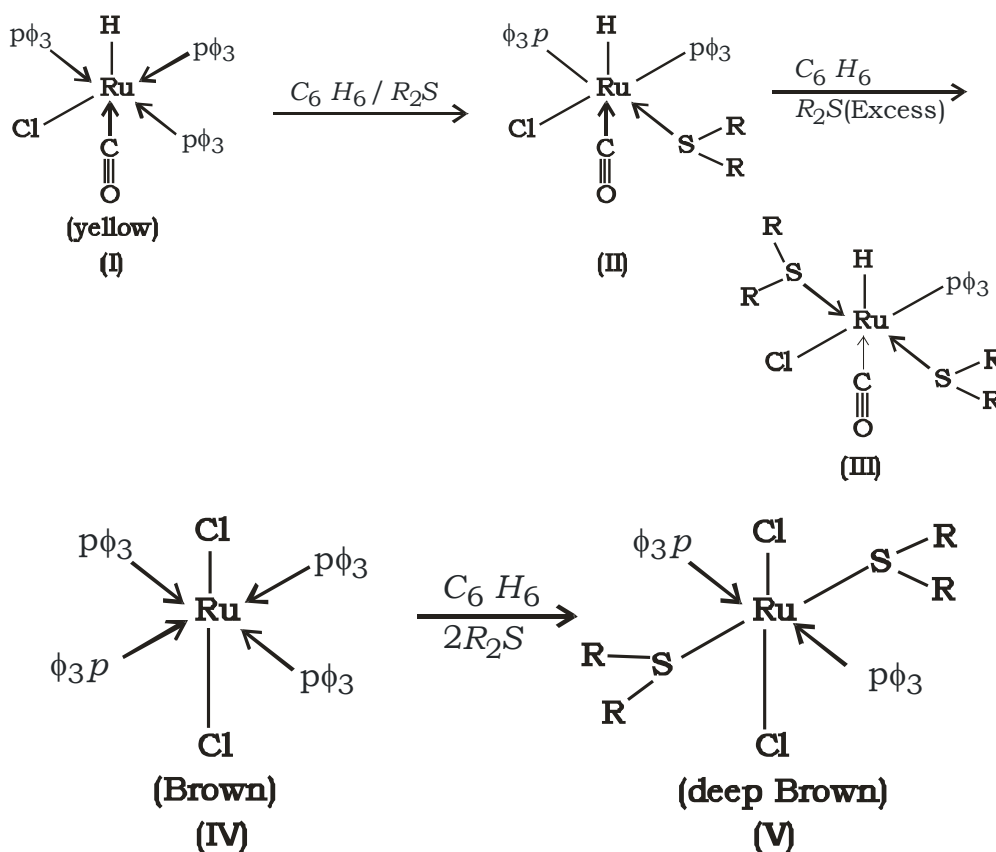
addition using 30% ethanolic solution of HCl. The mixture was stirred for 1 hr on magnetic stirrer and the solid products obtained are listed in table 1.

The IR spectra of the ligands and complexes were recorded on a Perkin-Elmer Model-577 Spectrophotometer in the range 4000-200 cm^{-1} as KBr pellets. The magnetic measurements were made on a gouy balance and the diamagnetic corrections for the ligand molecules were done. Electronic spectra of complexes were recorded on a Beckmann and Carl Zeiss (Jenna) spectrophotometer. The molar conductance of

complexes ($10^{-3}M$) were measured in DMF using Wiss-Werkstatter weitheim obb type LBR conductivity meter. ^1H and ^{31}P NMR spectra were recorded on Bruker 400 MHz or Varian FX90Q instruments using TMS and orthophosphoric acid as references respectively.

RESULTS AND DISCUSSION

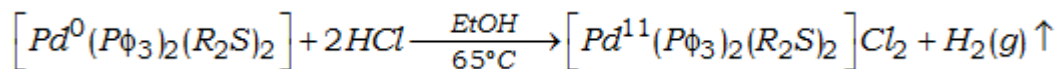
Light and air stable ruthenium(II) complexes were prepared by reacting with dibenzyl sulphide in a 1 : 1 molar ratio/excess of in benzene.



The ligand substitution in $[\text{RuH}(\text{CO})(\text{P}\phi_3)_3\text{Cl}]$ in benzene solution yields complex (III) easily but complex (IV) is formed under drastic conditions using excess dibenzyl sulphide or increasing time of stirring. However, bonded hydride ion as well as coordinated carbonyl group

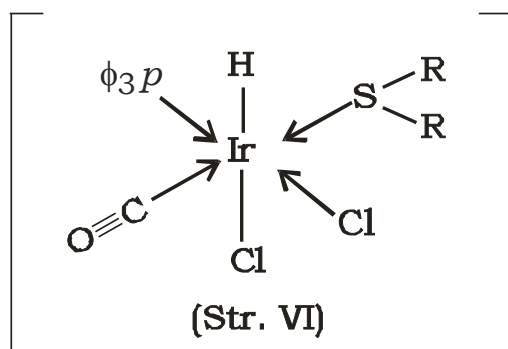
could not be replaced. Since CO group has much greater trans-effect than $\text{P}\phi_3$ and has greater trans effect than chlorine and the formation of str. III can be explained. The stephensen's compound under goes more easily ligand substitution giving Trans- (Str. V).

$[Pd(P\phi_3)_2(R_2S)_2]$ display oxidative addition reaction with ethanolic HCl as below:



The isolated product were 1 : 2 electrolyte and Na_2CO_3 -extract of complex produced total chlorine with $AgNO_3$ solution and supported molar conductance value. The Wilkinson catalyst $[Rh(P\phi_3)_3Cl]$ undergoes replacement in benzene and oxidative addition product with ethanolic HCl yields stable solid listed in Table 1.

Iridium (III) is a "b-class" acceptor which readily forms complexes with 'soft-sulphur' donor and incoming ligand takes up cis-position on oxidative addition to veska compound $[Ir(CO)(P\phi_3)_2Cl]$ after ligand substitution reaction was carried out (Str. VI).



Electronic spectra

The diamagnetic nature and electronic spectrum of $[Pd(P\phi_3)_2(R_2S)_2]Cl_2$ are indicative of square planar geometry. The spectra bands at $18450cm^{-1}$ and $27750cm^{-1}$ assigned to $1A_{1g} \rightarrow 1B_{1g}$ and $1A_{1g} \rightarrow 1E_g$ transitions and the band occurring at $34546cm^{-1}$ in UV region is ascribed to a charge transfer transition. Hence, a square planar geometry may be assigned for Pd(II) complex.¹⁷ The ruthenium (II) complexes were diamagnetic indicating ground state $1A_{1g}$ in

octahedral environment and two spin allowed transitions $1A_{1g} \rightarrow 1T_{1g}$ and $1A_{1g} \rightarrow 1T_{2g}$ are expected. The bands at $19670-19050 cm^{-1}$ and $18450-21275 cm^{-1}$ in all complexes are assigned to $1A_{1g} \rightarrow 1T_{1g}$ and $1A_{1g} \rightarrow 1T_{2g}$ respectively and other transition at $33890-34120 cm^{-1}$ is due to

. The nature of electronic spectra are similar to those observed for the other octahedral complexes.¹⁸ Hence, these complexes have similar octahedral structure as the parent compounds.

Rhodium (III) complex is diamagnetic and two spin-allowed transitions $1A_{1g} \rightarrow 1T_{1g}$ and $1A_{1g} \rightarrow 1T_{2g}$ and two spin-forbidden weak bands due to singlet-Triplet $1A_{1g} \rightarrow 3T_{1g}$ and $1A_{1g} \rightarrow 3T_{2g}$ transitions in octahedral field is expected.¹⁹ The spectral bands at $26300 cm^{-1}$ ($1A_{1g} \rightarrow 1T_{2g}$), $22500 cm^{-1}$ ($1A_{1g} \rightarrow 1T_{1g}$) and $17800 cm^{-1}$ ($1A_{1g} \rightarrow 3T_{1g}$) confirms octahedral structure considering previous literature.²⁰ The $[IrH(CO)(P\phi_3)(R_2S)Cl_2]$ also exhibits spectral bands at $26000 cm^{-1}$ ($1A_{1g} \rightarrow 1T_{2g}$), $22250 cm^{-1}$ ($1A_{1g} \rightarrow 1T_{1g}$) and $18450 cm^{-1}$ ($1A_{1g} \rightarrow 3T_{1g}$) are consistent with octahedral structure.²¹

IR Spectra

The IR bands of interest of the ligand, $P\phi_3$ and $R_2S(R = C_6H_5CH_2)$ and complexes are discussed here. A comparison of spectra of ligands and complexes indicate the formation of metal-S bond. The $\nu C-S$ band of dibenzylz sulphide shift from $720cm^{-1}$ to $680 \pm 5 cm^{-1}$ on complexation indicating the formation of metal-sulphur bond.²²⁻²⁴ The IR spectra of $R_2S, [Pd(P\phi_3)_2(R_2S)_2]Cl_2$ and $[Ru(P\phi_3)_2(R_2S)_2Cl_2]$ are almost identical in the range of $4000 cm^{-1}$ to $1500 cm^{-1}$. However, non-ligand bands at 2008 and $760 cm^{-1}$ in ruthenium complex (SL. No. 3) and at 2235 & $780 cm^{-1}$ for Ir

(III) complex (SL. No. 5 & 6) assigned to metal-H stretching mode and bending mode are in agreement with previous report.²⁵⁻²⁷ The presence of single metal-chlorine stretching mode in chloro complexes of ruthenium (II) complex (Sl. No. 2) suggest two chlorine at trans-position in octahedral structure. The presence of single Pd-S, Pd-P Ru-S, stretching modes also suggest transposition of two $P\phi_3$ group/or two R_2S molecules in octahedral geometry.

Deeming and shaw²⁸ and Farrel et al²⁹ have assigned ν Ir-Cl for Cl-Ir-CO at 330cm^{-1} . For $[IrH(CO)(P\phi_3)(R_2S)Cl_2]$ and $[IrH(CS)(P\phi_3)_2Cl_2]$ we observe ν Ir-Cl at 320cm^{-1} is in agreement with Kubota and Loeffler.³⁰ A value of 320cm^{-1} is border line between typical Cl-Ir-Cl and Cl-Ir-CO value.³¹

^1H NMR and ^{31}P NMR Spectra

The ligand to metal bonding is further supported by ^1H NMR spectra. $[Pd(P\phi_3)_2(R_2S)_2]Cl_2$ exhibits complex peak at $\delta 7.16-7.81\text{PPM}$ corresponding to aromatic protons of dibenzyl sulphide and two peaks centred at $\delta 4.5$ and 3.91PPM due to methylene (CH_2) protons. The shifting of the CH_2 proton signal to lower fields indicate coordination through sulphur.³² The signals in the $8.0-8.95\text{PPM}$ range due to the aromatic protons of $P\phi_3$.³³

The ^{31}P NMR spectra of Pd (II) complex exhibits a signal around $23.70-28.86\text{PPM}$ in the spectrum of complex confirmed the presence of magnetically equivalent phosphorous atoms and thus suggesting that the two $P\phi_3$ groups are trans to each other.³⁴ Thus, NMR spectral results are consistent with Ir Spectra.

Table 1: Analytical and physical data of complexes

S. No.	No. Complex/ (Colour)	Exp. Formula	Analysis % Found/(calcd)		
			C	H	Metal
1.	$[Pd(P\phi_3)_2(R_2S)_2]Cl_2$ (yellow)	$C_{64}H_{58}P_2S_2Cl_2Pd$	67.85 (67.99)	5.23 (5.13)	9.80 (9.42)
2.	$[Ru(P\phi_3)_2(R_2S)_2]Cl_2$ (Brown)	$C_{64}H_{58}P_2S_2Cl_2Ru$	68.12 (68.32)	5.32 (5.16)	9.11 (8.98)
3.	$[Ru(P\phi_3)_2(R_2S)_2]Cl_2$ (yellow)	$C_{47}H_{44}PS_2ClORu$	66.01 (65.92)	5.21 (5.14)	11.56 (11.80)
4.	$[RhH(P\phi_3)_2(R_2S)Cl_2]$ (yellow)	$C_{50}H_{45}P_2SCl_2Rh$	66.01 (65.72)	5.11 (4.92)	11.50 (11.27)
5.	$[IrH(CO)(P\phi_3)(R_2S)Cl_2]$ (yellow)	$C_{33}H_{30}PSCl_2OIr$	51.64 (51.54)	4.01 (3.90)	25.00 (25.02)
6.	$[IrH(CS)(P\phi_3)_2]Cl_2$ (Dull yellow)	$C_{37}H_{31}P_2SCl_2Ir$	55.51 (55.41)	3.92 (3.86)	24.01 (23.99)

$(R = C_6H_5CH_2-)$

Table 2: IR and Electronic spectra of complexes

Complex	Infrared Spectra (cm ⁻¹)				Electronic Spectra
	$V_{M-H} /$ -($\delta M-H$)	$V_{C\equiv X}$	V_{C-S}	$V_{M-Cl} /$ V_{M-S}	Bands (Assign (cm ⁻¹))
$[Pd(P\phi_3)_2(R_2S)_2]Cl_2$	-	-	680	385 (340)	34546 (CT Band) 18450 ($1A_1g \rightarrow 1E_1g$) 27750 ($1A_1g \rightarrow 1Eg$)
$[Ru(P\phi_3)_2(R_2S)_2Cl_2]$	- (-)	-	670	410 (305)	33890 (CT Band) 21275 ($1A_1g \rightarrow 1T_2g$) 19670 ($1A_1g \rightarrow 1T_1g$)
$[Ru H(CO)(P\phi_3)(R_2S)Cl]$	2008 (760) (305)	1980	690	430 & 410	34120 (CT Band) 20400 ($1A_1g \rightarrow 1T_2g$) 19050 ($1A_1g \rightarrow 1T_1g$)
$[Rh H(P\phi_3)_2(R_2S)Cl_2]$	2160 (410) (790)	-	700	460	34480 (CT Band) 26300 ($1A_1g \rightarrow 1T_2g$) 22500 ($1A_1g \rightarrow 1T_1g$) 17800 ($1A_1g \rightarrow 3T_1g$)
$[Ir H(CO)(P\phi_3)(R_2S)Cl_2]$	2235 (780)	2030	680	318 (302)	30300 ($T_2g \rightarrow \pi^*$) 26000 ($1A_1g \rightarrow 1T_2g$) 22250 ($1A_1g \rightarrow 1T_1g$) 18450 ($1A_1g \rightarrow 3T_1g$)
$[Ir H(CS)(P\phi_3)_2Cl_2]$	2240 (810)	2025	680	320 (295)	32000 ($T_2g \rightarrow \pi^*$) 27000 ($1A_1g \rightarrow 1T_2g$) 21000 ($1A_1g \rightarrow 1T_1g$) 17400 ($1A_1g \rightarrow 3T_1g$)

(X=O/S)

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