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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SOME HYDRIDOPHOSPHINE COMPLEXES OF IRIDIUM (III)

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ABSTRACT

Mononuclear hydridophosphine complexes of iridium (III) are prepared and characterized by elemental analyses, conductance, magnetic, IR, UV-vis and ^{1}H NMR spectral data. All complexes are found octahedral and two phosphine ligands are at trans-disposition. The ligand field bands are obscured in some cases. However, electronic spectral data is consistent with assigned structure.

Key words: Hydridophosphine complexes, Iridium (III), Trans-Oh, Spectra.

INTRODUCTION

Complexes of iridium are endowed with anticancer[1-3], antineoplastic[4], photochemical[5], liquid crystalline[6] and versatile catalytic properties[7-9]. They are currently attracting considerable attention due to their wide and diverse structural types and varied ligand bonding modes. In our earlier communication, we have reported organoiridium (I) complexes ligated with thioamides[10-14], amides[15] and other ligands[16]. The present communication is devoted to synthesis and spectroscopic properties of some novel hydridophosphine complexes of iridium (III) and their structural elucidation.

EXPERIMENTAL

All the chemicals used were CP grade or AR grade and were purchased from either Aldrich or Fluka and used as received. Solvents were distilled and dried before use. All complexes were prepared using a general method.

The suspension of $IrCl_3$ (0.05 mol), $P\phi_3$ (0.6 mol) and KCl (0.05 mol) in ethanol (100 mL) was stirred on magnetic stirrer at 85°C for 2 hr. The mixture was then allowed to

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evaporate on water-bath to half volume. The mixture was transferred into a beaker containing CS_2 or pyridine and stirred. The solid complexes obtained at pH = 6 were filtered and washed with methanol and dried over anhydrous $CaCl_2$ in a vacuum desiccator.

(1) Dichloridohydridotris (triphenyl phosphine) iridium (III)

$[IrHCl_2(P\phi_3)_3]$: Calculated (%) for $C_{54}H_{46}P_3Cl_2Ir$ (957.2): C = 67.69; H = 4.82; Ir = 20.07; Found (%): C = 68.10; H = 4.84; Ir = 20.01.

Dull yellow solid, M. P. = 125°C, diamagnetic, non-hygroscopic, non-conducting, soluble in DMF, DMSO, Insoluble in ether, C_6H_6, $CHCl_3$ and acetone.

(2) Dichloridohydridothiocarbonyl bis(triphenyl phosphine) iridium (III)

$[IrHCl_2(CS)(P\phi_3)_2]$: Calculated (%) for $C_{37}H_{31}P_2Cl_2SIr$ (832.2): C = 53.35; H = 3.72; Cl = 8.53; Ir = 23.09 Found (%): C = 53.63; H = 3.80; Cl = 8.62; Ir = 23.12

Light yellow solid, M. P. = 135°C, non-hygroscopic, non-conducting, soluble in DMF, Insoluble in ether, EtOH, C_6H_6, diamagnetic.

(3) Dichloridohydridopyridine bis(triphenyl phosphine) iridium (III)

$[IrHCl_2(Py)(P\phi_3)_2]$: Calculated (%) for $C_{41}H_{36}NP_2Cl_2Ir$ (867.2): C = 56.73; H = 4.15; Cl = 8.18; Ir = 22.16; Found (%): C = 57.01; H = 4.22; Cl = 8.38; Ir = 22.20.

Yellow solid, M. P. = 140°C, non-hygroscopic, non-conducting, diamagnetic, soluble in DMF, Insoluble in ether, EtOH, C_6H_6 and $CHCl_3$.

(4) Chloridohydridoditheiocarbonyl bis(triphenyl phosphine) iridium (III) chloride

$[IrHCl(CS)_2(P\phi_3)_2]Cl$: Calculated (%) for $C_{38}H_{31}S_2Cl_2P_2Ir$ (876.2): C = 52.04; H = 3.53; Cl = 8.10; Ir = 21.93; Found (%) : C = 52.10; H = 3.55; Cl = 8.20; Ir = 22.10

Traffic yellow coloured solid; M. P. = 180°C; non-hygroscopic, diamagnetic, Molar conductance (10^{-3} M) = 38.6 $\wedge^{-1}cm^2mol^{-1}$, soluble in EMK, acetone & DMF; Insoluble in ether, C_6H_6 and CCl_4.

(5) Chloridohydridotetra kis(triphenyl phosphine) iridium (III) chloride

$[IrHCl(P\phi_3)_4]Cl$: Calculated (%) for $C_{72}H_{61}P_4Cl_2Ir$ (1312.20): C = 65.84; H = 4.64; Cl = 5.41; Ir = 14.64; Found (%): C = 66.01; H = 4.72; Cl = 5.50; Ir = 14.66.

Pale cream solid, M. P. = 75°C, non-hygroscopic solid, diamagnetic, soluble in acetone, EMK & DMF, Insoluble in CCl_4, C_6H_6, EtOH & MeOH, Molar conductance 10^{-3} M DMF = 38.2 $\wedge^{-1}cm^2mol^{-1}$.

Carbon, hydrogen and nitrogen analyses were done at CDRI, Lucknw. Analysis of metal and chlorine were carried out using standard methods. Magnetic measurements were made by means of Gouy method at room temperature. The conductivity of complexes (10^{-3} M) in DMF was measured with the help of systronics conductivity meter. Infrared Spectra (KBr) were recorded one a Perkin-Elmer 621 spectrophotometer and electronic spectra (dioxane) on a Carl-Zeiss (Jena) Spectrophotometer. The ^1H NMR spectra were recorded on Bruker 400 MHZ instruments using TMS as internal indicator in the range of 0-10 PPM.

RESULTS AND DISCUSSION

All compounds were prepared by the reaction of triphenyl phosphine ($P\phi_3$) and $IrCl_3$ in ethanol and abstraction of hydride ligand occurs from ethanol. When reaction was carried out in CS_2 and ethanol mixture, abstraction of thiocarbonyl group also occurs. Analytical data supports their formulation. All complexes were non-electrolyte in DMF (10^{-3} M) indicating coordinated nature of chloride ion. However, molar conductance value of some complexes (4 & 5) were found between 38.2-38.6 $\wedge^{-1}cm^2mol^{-1}$ indicating uni-uni electrolytic nature and presence of ionic chloride[17]. All complexes were diamagnetic indicating trivalent iridium (d^6) in strong crystal field. Electronic spectra of complexes display only a single very strong band at 32785-32790 cm^{-1} due to charge transfer ($T_{2g} \rightarrow \pi^*$). The other ligand field bands are obscured probably due to high covalence.[18] However, two spin allowed transitions at 25210 and 29400 cm^{-1} in $[IrHCl_2(P_4)(P\phi_3)_2]$ are consistent with octahedral structure[19] and assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ respectively. One spin-forbidden transition band at 24215 cm^{-1} was also present and assigned to $^1A_{1g} \rightarrow {}^3T_{1g}$ transition.

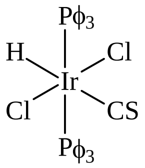
^{1}H NMR Spectra

The ^1H NMR spectra of $[IrHCl_2(P_y)(P\phi_3)_2]$ was recorded in $CDCl_3$/TMS to substantiate further mode of bonding. The complex exhibits signal in the range δ 8.12-8.80 PPM due to aromatic protons of coordinated $P\phi_3$. The resonances in the region δ 7.71 PPM, δ 8.20 PPM and δ 8.89 PPM assignable to the protons of Pyridine ligand along with the resonances due to aromatic protons of $P\phi_3$ and the integrated intensities of the signals agree with the assigned molecular formula.

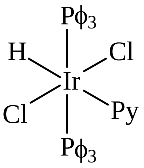
IR Spectra

The IR Spectrum of triphenyl phosphine ($P\phi_3$) has been interpreted by Deacon and Green[20]. Brown et al.[21] and Shobatake and co-workers[22] have observed metal-sensitive IR bands at 1089, 501, 428, 248 and 209 cm^{-1} in free $P\phi_3$ molecule. The strong bands around 1556, 740, 695 and 535 cm^{-1} in complexes indicated the presence of coordinated $P\phi_3$ molecules. A single band at 380-385 cm^{-1} confirmed the two $P\phi_3$ molecules are mutually trans in octahedral disposition and assigned to Ir-P stretching mode[23]. Since $P\phi_3$ exhibits a number of ligand vibration in the low-freqency region[24], the mixing of $P\phi_3$ vibrations may not be ruled out. The low value Metal-P stretching mode may be due to back-bonding in the M-P bond[25].

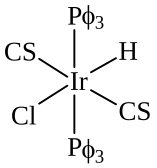
The non-ligand bands around 2000-2240 cm^{-1} and 810-830 cm^{-1} assigned to $\nu_{Ir\text{-}H}$ and $\delta_{Ir\text{-}H}$ modes consistent with previous assignments suggested by Chatt et al.[26] and Vaska[27]. The presence of single band at 320-325 cm^{-1} in the spectra of complexes suggests two chlorine at mutual trans in complexes (1, 2 & 3). Shaw and co-workers[29] suggested that the frequency of $\nu_{Ir\text{-}Cl}$ occurs in the range 320-303 cm^{-1} when trans ligand is chlorine, 278-262 cm^{-1} when it is $P\phi_3$ and 249-246 cm^{-1} when it is hydrogen. The strong band at 1370 cm^{-1} suggest C-bonded terminal CS group[30] in $[IrHCl(CS)_2(P\phi_3)_2]Cl$. Such band is not present in other complexes.



(S. No. 2)
ν Ir-Cl = 325 cm^{-1}



(S. No. 3)
ν Ir-Cl = 319 cm^{-1}



(S. No. 1)
ν Ir-Cl = 220 cm^{-1}

Table 1: Major infrared spectral bands of complexes (cm^{-1})

Complex/(Colour, M. P. ^{0}C)	ν Ir – H	δ Ir – H	ν Ir – Cl	ν Ir – P
$[IrHCl_2(P\phi_3)_3]$ (dull yellow, 125)	2195 (ms)	840 (m) 805 (m)	320 (m)	380 (m)
$[IrHCl_2(CS)(P\phi_3)_2]$ (light yellow, 135)	2000 (s)	830 (m)	325 (m)	385 (m)

Cont…

Complex/(Colour, M. P. ^{0}C)	**ν Ir – H**	**δ Ir – H**	**ν Ir – Cl**	**ν Ir – P**
$[IrHCl_2(P_4)(P\phi_3)_2]$ (yellow, 140)	2240 (s)	810 (m)	320 (m)	382 (m)
$[IrHCl(CS)_2(P\phi_3)_2]Cl$ (Traffic yellow, 180)	2230 (m)	815 (m)	248 (m)	385 (m)
$[IrHCl(P\phi_3)_4]Cl$ (Pale Cream, 75)	2235	810 (m)	280	383 (m)

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