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Synthesis and Characterization of Platinum Group Metal Complexes of Diphenylphosphinoacetic Acid

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Abstract

Complexes of diphenylphosphinoacetic acid (POH) with platinum group metal ions are reported. Reaction of an excess of POH with the rhodium(I) complex $RhCl(PPh_3)_3$ resulted in the formation of the octahedral Rh(III) complex *fac*-$Rh(PO)_3$ by the oxidative addition of protons to the Rh(I) species. Reaction of $RhCl(PPh_3)_3$ with POH in a 1:2 molar ratio however, gave the square planar Rh(I) complex $Rh(PO)(POH)(PPh_3)$. Interaction of POH with the Rh(I) and Ir(I) square planar complex $MCl(CO)(PPh_3)_2$ in a 2:1 molar ratio gave complexes of the type *trans*-M(PO)(POH)(CO). The reaction of $PdCl_2(C_6H_5CN)_2$ and K_2PtCl_4 with POH in a 1:2 molar ratio gave complexes of the composition *cis*-M(PO)(POH)Cl. Interaction of $RhCl_3$ and $IrCl_3$ with POH in a 1:3 molar ratio resulted in the formation of complexes of the type $M(PO)_2(POH)Cl$ (M = Rh(III) and Ir(III)). The complexes were characterized by ^1H, ^{13}C, ^{31}P, NMR and IR spectroscopy.

Introduction

In recent years considerable attention has been focussed on the complexes of platinum group metal ions with functionalized tertiary phosphines [1], because of their use as homogeneous catalysts [2]. Recently, we have synthesized platinum group metal complexes with potential bidentate and terdentate ligands, containing hybrid donor atoms [3] and studied their catalytic activity in the homogeneous hydrogenation of olefins [4]. The bidentate ligand, diphenylphosphinoacetic acid [5, 6] contains hybrid phosphorous and oxygen donor atoms, phosphorus being a good π-acidic and carboxylate oxygen a basic σ-donor. The ligand is thus expected to maintain a fine balance of electron density on being coordinated to soft platinum group metal ions with filled d-orbitals of low electronegativity. In such complexes, the carboxylate group is expected to stabilize the positive charge on the metal ions and help those reactions that proceed by a polarization mechanism of separation of charges.

There have been few studies however on hybrid ligands containing phosphorus and oxygen with platinum group metal ions [1, 7]. The present paper deals with the synthesis of platinum group metal complexes with diphenylphosphinoacetic acid (POH) and their characterization by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy.

Experimental

Physical Measurements

Elemental analyses of the complexes were performed by Australian Mineral Development Laboratories (AMDEL), Australia. Melting points and conductivity measurements were done as reported [8]. Infrared spectra of the solid complexes were recorded on Beckman IR-12 spectrometer, as KBr pellets. Far-infrared spectra (600–100 cm^{-1}) were recorded on a Nicolet 200SXV FT-IR Spectrometer. The far-infrared spectra of the complexes were obtained in Nujol mulls pressed between polyethylene films. ^1H NMR spectra of the complexes were taken on a Jeol FX-100 FT-NMR in the indicated solvents, operating at 99.55 MHz. The $^{31}P\{^1H\}$ NMR spectra were recorded at 40.27 MHz in the indicated solvents using spinning 10 mm tubes with a capillary of deuterium oxide for the internal lock and 85% H_3PO_4 as an external standard. Positive chemical shifts are downfield from the H_3PO_4 standard. $^{13}C\{^1H\}$ NMR spectra were recorded in the indicated solvents at 24.99 MHz. Tetramethylsilane was used as an external reference. The electronic spectra of complexes were measured in DMSO and chloroform on a Shimadzu UV-240 spectrometer.

Materials

Organic solvents were reagent grade and were deoxygenated with purified nitrogen prior to use. $RhCl_3 \cdot 3H_2O$, $IrCl_3 \cdot 3H_2O$, $PdCl_2$ and K_2PtCl_4 were

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TABLE I. Analytical and Conductivity Data of the Complexes

Complex[a]	Colour	Melting point[b] (°C)	Conductivity[c] (ohm^{-1} cm^2 mol^{-1})	Elemental analysis (%)[d]			
				C	H	P	Cl
1 Rh(PO)$_3$	pale yellow	176–178	12(C)	59.95 (60.58)	4.30 (4.36)	11.05 (11.18)	–
2 Rh(PO)(POH)(PPh$_3$)	cream	195–198	11(C)	65.00 (64.79)	4.76 (4.73)	11.02 (10.91)	–
3 Rh(PO)(POH)(CO)	pale yellow	175–178	12(C)	56.50 (56.31)	4.11 (4.08)	10.09 (10.03)	–
4 Rh(PO)$_2$(POH)Cl	pale yellow	218–220	15	57.98 (58.03)	4.32 (4.29)	10.68 (10.71)	4.01 (4.09)
5 Ir(PO)(POH)(CO)	white	210–213	13(C)	48.93 (49.21)	3.63 (3.56)	8.84 (8.76)	–
6 Ir(PO)$_2$(POH)Cl	cream	155–160	19(C)	53.01 (52.62)	3.77 (3.89)	9.84 (9.86)	3.68 (3.71)
7 Pd(PO)(POH)Cl	yellow	200–203	25	52.90 (53.42)	4.09 (4.00)	10.00 (9.86)	5.76 (5.64)
8 Pt(PO)(POH)Cl	gray	230–234	10	46.98 (46.82)	3.60 (3.51)	3.64 (8.64)	5.00 (4.95)

[a] POH = diphenylphosphinoacetic acid, PO = diphenylphosphinoacetate. [b] Decomposition temperature. [c] Conductivity measurements were done in DMSO at room temperature except where mentioned C = chloroform. [d] Calculated values are given in parentheses.

obtained from Johnson Matthey (U.K.) and Alfa Inorganic (U.S.A.). The ligands triphenylphosphine and triphenylarsine were purchased from Strem Chemicals Inc. (U.S.A.). The complexes RhCl(PPh$_3$)$_3$ [9], Rh(Cl(CO)(PPh$_3$)$_2$ [10], IrCl(CO)(PPh$_3$)$_2$ [10, 11] and the ligand diphenylphosphineacetic acid were prepared by reported procedures [5, 6].

Preparation of the Complexes

All preparations were carried out under nitrogen. Microanalytical data, conductivity and melting point data are presented in Table I. The IR and electronic spectral data are presented in Table II.

Synthesis of Metal Complexes

fac-Tris(diphenylphosphinoacetato)rhodium(III), Rh(PO)$_3$ (1)

The ligand POH (0.180 g, 0.75 mmol) was added to a solution of RhCl(PPh$_3$)$_3$ (0.200 g, 0.216 mmol) in benzene when the reddish colored solution turned to yellowish orange. The solution was refluxed until crystallization of the product commenced and the mixture was then allowed to cool to room temperature. The crystals were filtered off, washed with warm benzene and dried *in vacuo*. Recrystallization of the complex was done from acetone-n-hexane. (Yield: 78%.)

(Diphenylphosphinoacetato)(diphenylphosphinoacetic acid)triphenylphosphinerhodium(I), [Rh(PO)(POH)(PPh$_3$)] (2)

To a benzene solution of RhCl(PPh$_3$)$_3$ (0.30 g, 0.24 mmol) 0.58 g, (0.648 mmol) of POH was added when the reddish brown coloured solution instantaneously changed to light yellow. The resulting solution was refluxed for an additional two hours and the reaction mixture concentrated to a small volume. The complex was precipitated by the addition of diethyl ether, filtered off, washed with ether and recrystallized from CHCl$_3$-n-hexane and dried *in vacuo*. (Yield: 70%.)

(Diphenylphophinoacetato)(diphenylphosphinoacetic acid)carbonylrhodium(I), [Rh(PO)(POH)(CO)] (3)

A solution of Rh(Cl)(CO)(PPh$_3$)$_2$ (0.250 g, 0.362 mmol) in benzene (30 ml) was treated with POH (0.18 g, 0.72 mmol) and the resulting mixture refluxed for two hours. The yellow crystals that separated were filtered, washed with warm benzene and recrystallized from chloroform-n-hexane. (Yield: 80%.)

Chlorobis(diphenylphosphinoacetato)(diphenylphosphinoacetic acid)rhodium(III), [RhCl(PO)$_2$(POH)] (4)

POH (0.278 g, 1.14 mmol) was dissolved in (30 ml) ethanol and the solution added to an ethanolic

TABLE II. Infrared[a] and Electronic[b] Spectral Data

	Complex[c]	ν(M–Cl)[d]	ν(M–P)	ν(COO)[e]	ν(M–CO)	λ_{max}, (nm)[f] (ϵ_{max})
1	$Rh(PO)_3$		548(vs)	1600(s)		192(9500), 218(10990), 243(15690), 274(20350), 557(15), 605(13)
2	$Rh(PO)(POH)(PPh_3)$		529(s) 512(s)	1670(b) 1550(s)		245(19970), 267(23010), 376(750), 488(180), 566(35), 644(16), 750(12)
3	Rh(PO)(POH)(CO)		516(vs)	1720(s) 1600(b)	1980(s)	199(13080), 243(17200), 275(19500), 488(170), 557(43), 518(19), 645(12)
4	$Rh(PO)_2(POH)Cl$	332(vs)	520(s)	1680(b) 1600(b)		244(15150), 268(29370), 431(480), 487(410), 576(22), 631(21)
5	Ir(PO)(POH)(CO)		502(vs)	1710(s) 1600(b)	2010(vs)	203(1663), 226(1606), 262(132), 488(33), 557(20)
6	$Ir(PO)_2(POH)(Cl)$	321(s)	507(sh) 501(vs)	1700(vs) 1580(s)		237(13680), 267(27820), 480(270), 712(5)
7	Pd(PO)(POH)Cl	305(s)	508(b)	1710(s) 1598(vs)		250(15960), 273(17650), 588(15)
8	Pt(PO)(POH)Cl	314(s)	530(vs)	1715(s) 1605(vs)		269(3643), 377(76), 487(89), 712(23)

[a] Absorptions are in cm^{-1}, vs = very strong, s = strong, b = broad, sh = shoulder. [b] Electronic spectra recorded in DMSO/$CHCl_3$. [c] $PO = Ph_2PCH_2COO^-$; $POH = Ph_2PCH_2COOH$. [d] Measured in polyethylene films. [e] Measured in KBr discs. [f] Molar extinction coefficient values (ϵ (M^{-1} cm^{-1})) are given in parentheses.

solution of $RhCl_3$ (0.10 g, 0.38 mmol). The resulting mixture was refluxed until crystallization of the product commenced. The mixture was then allowed to cool to room temperature. The crystals of the complex were filtered off, washed with warm ethanol and recrystallized from DMSO. (Yield: 70%.)

(Diphenylphosphinoacetato)(diphenylphosphinoacetic acid)carbonyliridium(I), [Ir(PO)(POH)(CO)] (5)

A solution of chlorobis(diphenylphosphine)carbonyliridium(I) (0.22 g, 0.282 mmol) in benzene (20 ml), was treated with POH (0.138 g, 0.57 mmol). The resulting mixture was refluxed for 6 h and the white crystalline precipitate filtered off, washed with warm benzene, recrystallized from acetone and dried *in vacuo*. (Yield: 80%.)

Chlorobis(diphenylphosphinoacetato)(diphenylphosphinoacetic acid)iridium(III), [IrCl(PO)(POH)] (6)

Trichloroiridium(III) trihydrate (0.177 g, 0.5 mmol) was dissolved in ethanol and treated with POH (0.39 g, 1.5 mmol). The colour of the solution changed to greenish orange and finally to light yellow. The reaction mixture was refluxed for 4–5 h and the solution concentrated to a small volume on roto-evaporator. The cream coloured complex was precipitated by addition of petroleum ether, filtered off, washed with petroleum ether and recrystallized from dichloromethane. (Yield: 65%.)

Chloro(diphenylphosphinoacetato)(diphenylphosphinoacetic acid)palladium(II), [PdCl(PO)(POH)] (7)

A solution of $PdCl_2(C_6H_5CN)_2$ (0.20 g, 0.52 mmol) in benzene was treated with POH (0.254 g, 1.04 mmol). The brown solution of the palladium complex changed to yellow with the separation of yellow crystals which were filtered off, washed with benzene and dried *in vacuo*. (Yield: 93%.)

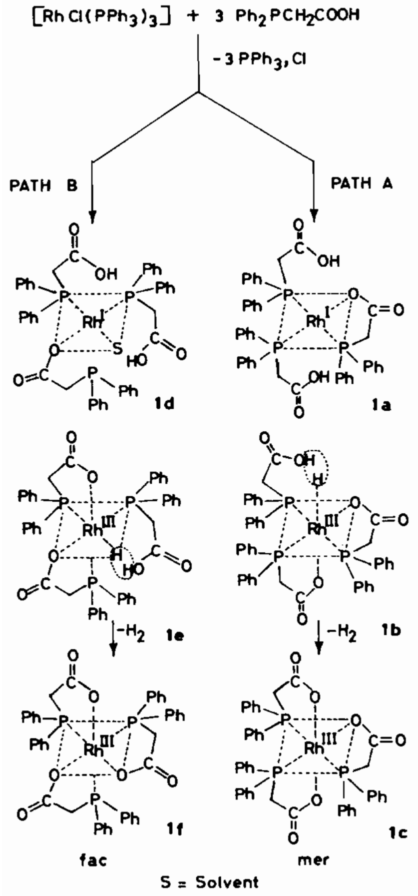
Chloro(diphenylphosphinoacetato)(diphenylphosphinoacetic acid)platinum(II), [PtCl(PO)(POH)] (8)

K_2PtCl_4 (0.200 g, 0.482 mmol) was dissolved in 1:1 water:methanol mixture and treated with POH (0.24 g, 0.96 mmol). The reddish colour of K_2PtCl_4 solution changed to yellow and finally to gray with the formation of shining gray crystals. The crystals were filtered off, washed with methanol and dried *in vacuo*. (Yield: 96%.)

Results and Discussion

The rhodium(I) complex $RhCl(PPh_3)_3$ on reflux in benzene with POH in a 1:4 ratio gave the rhodium(III) complex of the composition $Rh(PO)_3$ (**1**). The conductivity of complex **1** in chloroform and methanol (Table I) shows the complex to be a non-electrolyte [12]. In the formation of complex **1** oxidative addition of Rh(I) to Rh(III) takes place in the presence of an excess of the ligand POH. This is expected since the ligand substitution and oxidative addition reaction of Rh(I) complexes often proceed through coordinatively unsaturated 16 electron intermediates [13]. The 16 electron intermediate should be nucleophilic and should undergo a facile oxidative addition reaction. It is known that Rh(I) and Ir(I) act as nucleophiles, and the tendency to undergo oxidative addition is enhanced by decreasing the bulk and increasing the σ-donor capacity of the coordinated ligand, which results in an increase of electron density on the metal ion. In bulky ligands such as P^tBu_3 and P^tBu_2Pr steric factors are dominant and these ligands give very stable nd^8 M(I) complexes [13, 14]. Complexes like $RhCl(PPh_3)_3$ are very reactive in oxidative addition reactions particularly in the presence of organic acids [15]. Thus $RhCl(PPh_3)_3$ can undergo an oxidative addition reaction in the presence of an excess of diphenylphosphinoacetic acid to give $Rh(PO)_3$. A tentative reaction route for the formation of Rh(III) complex **1** from Rh(I) by an oxidative addition of proton from POH is given in Scheme 1.

Reaction of $RhCl(PPh_3)_3$ with POH in excess, forms intermediates **1a** and **1d** with one bidentate and two monodentate POH in **1a** and three mono-



Scheme 1.

TABLE III. $^{31}P\{^1H\}$ NMR Spectral Data[a] of Platinum Group Metal Complexes

	Complex[b]	Solvent	Spectrum[c] type	Chemical shifts (ppm)[d]			Coupling constants (Hz)				
				P_a	P_b	P_c	$^1J(M-P_a)$	$^1J(M-P_b)$	$^2J(P_a-P_b)$	$^2J(P_a-P_c)$	$^2J(P_b-P_c)$
1	$Rh(PO)_3$	CH_2Cl_2	AX	10.87(d)			115				
2	$Rh(PO)(POH)(PPh_3)$	CH_2Cl	ABCX	47.68 (ddd)	24.31 (ddd)	19.01 (ddd)	170	189 $^1J(M-P_c) = 130$	110	34	18
3	$Rh(PO)(POH)(CO)$	CH_3OH	ABX	13.43(t)	12.50(t)		115	118	34		
4	$Rh(PO)_2(POH)Cl$	Me_2SO	B_2AX	19.46(d)	24.67(d)		110	112			
5	$Ir(PO)_2(POH)(CO)$	$CHCl_3$	AB	−17.04(d)	−20.25(d)				37		
6	$Ir(PO)_2(POH)Cl$	$CHCl_3$	AB_2	−14.77(t)	−16.22(d)				24		
7	$Pd(PO)(POH)Cl$	Me_2SO	AB	21.92	12.11						
8	$Pt(PO)(POH)Cl$	Me_2SO	ABX	1.21(d)	−5.69(d)		3520	3720	15		

[a] $J \pm 0.3$ Hz. [b] $PO = Ph_2PCH_2COO^-$; $POH = Ph_2PCH_2COOH$. [c] $X = {}^{103}Rh/{}^{195}Pt$. [d] The chemical shift values (δ) are in ppm relative to 85% H_3PO_4 with positive values downfield from the standard, s = singlet; d = doublet; t = triplet; ddd = doublet of doublets of doublets.

dentate [9] POH in **1d** coordinated to Rh(I), respectively (paths A and B) (Scheme 1).

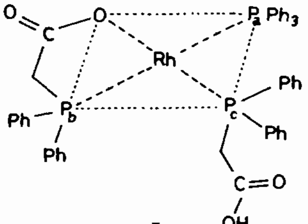
The strong σ-donor carboxylate lowers the activation energy required for an oxidative addition reaction from the proton of POH. Thus intermediate hydrido complexes **1b** and **1e** are formed in paths A and B, respectively. The intermediate Rh(III) hydrido complexes **1b** and **1e** then react with a proton from the monodentate POH with the elimination of molecular hydrogen and formation of the meridional and facial Rh(III) complexes **1e** and **1f**, respectively. The isomer actually isolated however, is the facial one **1e** which shows that path B takes priority over path A in the formation of **1**.

The infrared spectrum of complex **1** (Table II) shows a strong band at 1600 cm^{-1} assigned to coordinated $\nu(COO^-)$ group. The band at 548 cm^{-1} can be assigned to ν(Rh–P) stretching frequency.

The proton decoupled ^{31}P NMR of complex **1** (Table III) shows an AX type of spectrum, (X = ^{103}Rh, 100% abundance of spin 1/2) with a strong doublet centered at 10.87 ppm with $^1J(Rh-P) = 115$ Hz. The presence of the doublet shows that complex **1** exists in a facial geometry. The ^{13}C and ^1H NMR spectra support the assigned geometry of complex **1** (Table IV).

The reaction of $RhCl(PPh_3)_3$ with POH in a 1:2 molar ratio in benzene gave a cream coloured complex of the composition Rh(PO)(POH)(PPh_3) (**2**). The conductivity of complex **2** in dichloromethane and acetone shows (Table I) the complex to be non-electrolyte [12]. The infrared spectrum of complex **2** (Table II) shows bands at 1670 and 1550 cm^{-1} which are assigned to uncoordinated and coordinated ν(COO) groups, respectively. The bands at 539 and 512 cm^{-1} are assigned to ν(Rh–P) of PO and PPh_3, respectively.

The $^{31}P\{^1H\}$ NMR spectrum of complex **2** shows an ABCX pattern. The spectrum clearly shows three doublet of doublets of doublets centered at 47.68, 24.31 and 19.01 ppm which are assigned to the resonances of P_a, P_b, P_c ^{31}phosphorus atoms (structure **I**), respectively. The coupling constants between rhodium and phosphorus atoms are $^1J(Rh-P_a) = 170$, $^1J(Rh-P_b) = 189$ and $^1J(Rh-P_c) = 130$ Hz with second order coupling $^2J(P_a-P_b) = 110$, $^2J(P_a-P_c) = 34$ and $^2J(P_b-P_c) = 18$ Hz, respectively.



I

Treatment of a benzene solution of Rh(Cl)(CO)(PPh_3)$_2$ with POH in a 1:2 molar ratio gave a complex of the composition Rh(PO)(POH)CO (**3**). The conductivity of complex **3** in chloroform and DMSO (Table I) shows that the complex is a non-electrolyte [12]. The infrared spectrum of complex **3** (Table II) shows a strong band at 1980 cm^{-1} assigned to coordinated ν(CO). The peaks at 1720 and 1600 cm^{-1} in the carboxyl region are assigned to ν(COOH) and $\nu(COO^-)$, respectively.

The proton decoupled ^{31}P NMR spectrum of complex **3** (Fig. 1) shows an ABX pattern (Table III). The peaks centered at 13.43 and 12.50 ppm are assigned to phosphorus atoms P_a and P_b, respectively (structure **II**). The Rh–P coupling constants are $^1J(Rh-P_a) = 115$ and $^1J(Rh-P_b) = 118$ Hz, and the *trans* phosphorus coupling constant $^2J(P_a-P_b)$ is 34 Hz. An

TABLE IV. ^1H NMR Data[a]

Complex[b]		Solvent	^1H Chemical shifts[c]		
			Phenyl	PO (CH_2)	POH (CH_2)
1	Rh(PO)$_3$	$CDCl_3$	7.75(m)	3.73(d) (6.0)	
2	Rh(PO)(POH)(PPh_3)	$CDCl_3$	7.80(m) 7.26(m)	3.90(s)	3.21(s)
3	Rh(PO)(POH)(CO)	$CDCl_3$	7.70(b)	3.67(b)	3.35(b)
4	Rh(PO)$_2$(POH)Cl	DMSO-d_6	7.69(b)	3.63(s)	3.16(s)
5	Ir(PO)(POH)(CO)	$CDCl_3$	7.44(t) (10.0)	3.58(d) (6.25)	3.11(d) (6.59)
6	Ir(PO)$_2$(POH)(Cl)	$CDCl_3$	7.52(m)	3.60(d) (6.88)	3.29(d) (6.60)
7	Pd(PO)(POH)(Cl)	DMSO-d_6	7.64(m)	3.61(d)	3.20(d)
8	Pd(PO)(POH)(Cl)	DMSO-d_6	7.33(b)	3.37(s)	3.15(s)

[a] Values are reported in ppm relative to Me_4Si. [b] PO = $Ph_2PCH_2COO^-$; POH = Ph_2PCH_2COOH. [c] b = broad; d = doublet; m = multiplet; s = singlet; t = triplet.

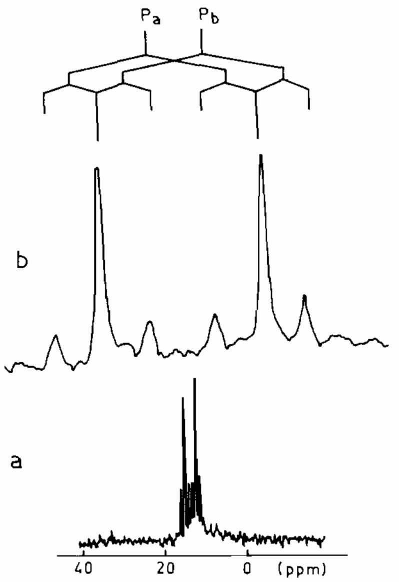
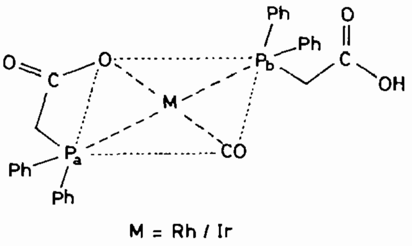


Fig. 1. The $^{31}P\{^1H\}$ NMR spectrum of (a) Rh(PO)(POH)(CO) at 23 °C in CH_3OH; (b) the peaks shown on an expanded scale.

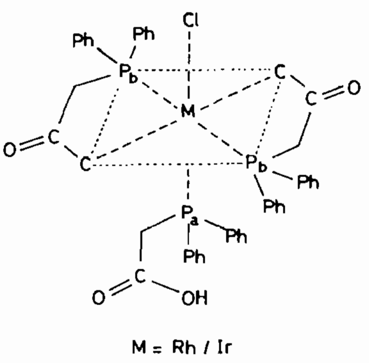


II

interesting feature of this ^{31}P spectrum is the fact that the two phosphorus atoms P_a and P_b are *trans* to each other [7] with almost the same chemical environment. Thus the difference between the two chemical shifts is 0.93 ppm. One would have expected an ABX spectrum to give doublet of doublet but complex **3** gives two triplets. This is explained on the basis of the fact that the interaction of rhodium spin (1/2) with P_a and P_b resonance gives initially two doublets. The second order splitting then gives the two triplets by the overlap of the shoulders with an intense middle peak.

The $^{13}C\{^1H\}$ NMR spectrum of **3** clearly shows a peak at 217.16 ppm which can be assigned to carbonyl carbon in the complex. The peaks at 200.96 and 175.51 ppm in the carbonyl region can be assigned to coordinated and uncoordinated carboxylate groups, respectively. The peaks in the aromatic and aliphatic region are given in Table IV.

Complex **4** was obtained by the reaction of $RhCl_3{\cdot}3H_2O$ with POH in a 1:3 molar ratio under reflux in alcohol. The conductivity of complex **4** in DMSO shows that the complex is a non-electrolyte



III

[12] (Table I). The analytical and spectroscopic data are consistent with the proposed structure **III**. The infrared spectrum shows peaks at 1680 and 1600 cm^{-1} assigned to uncoordinated and coordinated ν(COO) stretching frequencies, respectively. The two strong absorption bands at 520 and 332 cm^{-1} are assigned to ν(Rh–P) and ν(Rh–Cl) frequencies, respectively (Table II).

The $^{31}P\{^1H\}$ NMR of complex **4** (Table III) exhibits an B_2AX pattern. The doublets centered at 24.67 and 19.46 ppm with $^1J(Rh–P_b) = 112$ and $^1J(Rh–P_a) = 110$ Hz are assigned to phosphorus atoms P_b and P_b, respectively (structure **III**).

The P_a phosphorus atom which is *trans* to chloride should experience a large downfield shift as compared to P_b atoms which are *trans* to each other. One would have expected an AB_2 pattern for this complex, but the observed spectrum clearly shows a B_2AX type spectrum which can be explained on the basis of the chelate effect [16] to be more predominant than the *trans* chloride effect in this complex. The apparent absence of $^2J(P_a–P_b)$ in the B_2A pattern cannot be explained by a satisfactory model. Similar observations of a zero coupling in rhodium(I) complexes are reported by Meek *et al.* [17].

The treatment of a benzene solution of Ir(CO)(Cl)$(PPh_3)_2$ with POH in a 1:2 molar ratio gave a white crystalline iridium(I) complex of the composition Ir(CO)(PO)(POH) (**5**). The conductivity [12], analytical data and IR data of the complex are given in Tables I and II, respectively. The structure of complex **5** is similar to that of complex **3**.

The $^{31}P\{^1H\}$ NMR of complex **5** (Table III) shows an AB type of spectrum with doublets centered at −17.04 and −20.25 ppm, and with $^2J(P_a–P_b) = 37$ Hz. The coordination chemical shifts ($\Delta(\delta$ complex − δ ligand)) −1.06 and −4.27 ppm are assigned to phosphorus atoms P_a and P_b, respectively (structure **II**). The ^{31}P chemical shifts in coordination compounds are usually observed downfield as compared to that of the free ligand, mainly due to the strong σ-donor bond from phosphorus to metal with small

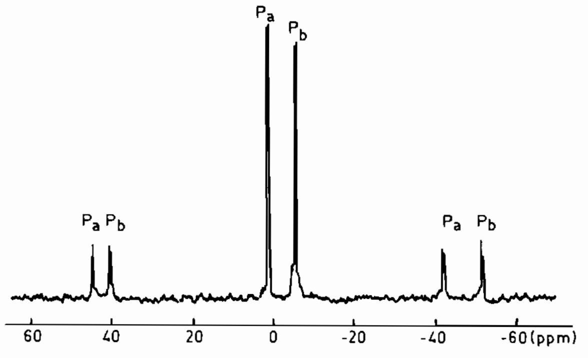


Fig. 2. The $^{31}P\{^1H\}$ NMR spectrum of *cis*-Pt(POH)Cl in DMSO at 23 °C.

d_π–d_π back donation from the metal ion to phosphorus. The upfield shift in the case of heavier transition metal ions like Ir(I) can be accounted for in terms of a weaker σ-donation of phosphorus to the metal ion and a strong metal–ligand d_π–d_π back bonding interaction. In the group Co(I), Rh(I) and Ir(I) [18] the coordination chemical shift is highest for the first member of the series Co(I) and decreases in the order Co(I) > Rh(I) > Ir(I) in line with an increase in the size and decrease in the electronegativity of the metal ion. The chemical shifts of the third row transition metals usually lie either close to the free ligand value or at values more upfield to that of the free ligand [19, 20]. On the basis of the above considerations high field coordination chemical shifts in iridium complexes are expected.

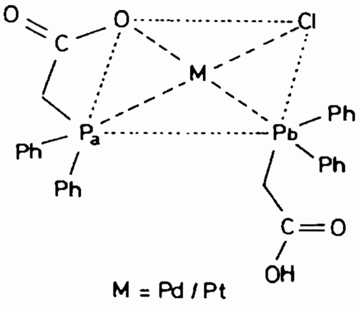
The interaction of POH with $IrCl_3 \cdot 3H_2O$ in a 3:1 molar ratio gave complex **6** which is similar in structure to complex **4** (structure **III**). The analytical conductivity and IR data of complex **6** are given in Tables I and II, respectively.

The proton decoupled ^{31}P NMR spectrum of complex **6** exhibits an AB_2 pattern. The triplet centered at −14.77 and the doublet centered at −16.22 ppm with $^2J(P_a–P_b) = 24$ Hz can be assigned to P_a which is *trans* to chloride [21, 22] and P_b atoms which are *trans* to each other, respectively.

Interaction of Rh(III) and Ir(III) with POH in a 1:3 molar ratio forms distorted octahedral complexes with two POH coordinated to the metal ion as a bidentate ligand through phosphorus and oxygen and one POH coordinated in a monodentate manner through phosphorus. The sixth coordination position on the metal ion is occupied by chloride (structure **III**). There is a good correlation between the size of the metal ion and the upfield chemical shifts of P_a and P_b phosphorus atoms which decrease in the order Rh(III) > Ir(III). The shielding effect is very pronounced in the 5d metal ion Ir(III).

Complexes **7** and **8** were obtained by the reaction of POH with $PdCl_2(C_6H_5CN)$ and K_2PtCl_4, respectively in a 1:2 molar ratio under reflux in benzene and 1:1 H_2O–methanol mixtures. The analytical, conductivity and infrared spectral data of the complexes are given in Tables I and II, respectively [23].*

The $^{31}P\{^1H\}$ NMR spectrum of **7** shows an AB type of spectrum [21, 22]. The downfield peak at δ21.92 is assigned to P_a which is *trans* to chloride (structure **IV**). The upfield peak at 12.11 ppm is assigned to phosphorus atom P_b. The apparent absence of *cis* $^2J(P_a–P_b)$ [24] coupling may be due to the low magnitude of $^2J(P–P)$ which is reduced to a point where it is less than the natural line width of the spectral line and therefore undetected.



IV

The $^{31}P\{^1H\}$ spectrum of complex **8** (Table III) shows an AB type of spectrum with ^{195}Pt side bands. The two doublets centered at 1.21 and −5.69 ppm with ^{195}Pt satellites are assigned to P_a and P_b phosphorus atoms, respectively. The downfield shift of P_a is due to its *trans cis* position to chloride. The observed coupling constants are $^1J(Pt–P_a) = 3520$, $^1J(Pt–P_b) = 3720$ and $^2J(P_a–P_b) = 15$ Hz. The platinum phosphorus coupling constants were calculated from the ^{195}Pt satellites. The large value of platinum phosphorus coupling constants and small values of $^2J(P–P)$ show that the phosphorus atoms are in a *cis* configuration [19, 25].

The proton, $^{13}C\{^1H\}$ NMR and electronic spectral data of complexes **1** to **8** are given in Tables IV, V and II, respectively. In the electronic spectra of complexes **1**–**8** the intense bands with high molar extinction coefficient values (Table II) in the range 192–300 nm may be assigned to ligational transitions. The bands with low molar extinction coefficient values are assigned to d–d transitions.

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*Complexes 7 and 8 were reported by Shaw *et al.* [23]. However, the experimental conditions and the starting complex for 8 was different. Shaw *et al.* [23] have proposed *trans* geometry on the grounds of infrared spectra solely.

TABLE V. $^{13}C\{^1H\}$ NMR Data[a]

	Complex[b]	Solvent	^{13}C Chemical shifts[c]					
			Methylene		Phenyl	Carboxyl		Carbonyl
			PO	POH		PO	POH	
1	$Rh(PO)_3$	$CDCl_3$	39.43(s)		132.98(m)	205(d) (10.63)		
2	$Rh(PO)(POH)(PPh_3)$	$CDCl_3$	42.0(s)	36.0(s)	133.67(m) 128.53(m)	207.95(s)	176.05(s)	
3	$Rh(PO)(POH)(CO)$	$CDCl_3$	38.94(s)	35.67(s)	132.46(m)	200.96(s)	175.51(s)	217.16(s)
4	$Rh(PO)_2(POH)Cl$	DMSO	39.43(d) (19.52)	36.01(d) (16.07)	133.34(m)	198.09(s)	177.44(d) (8.83)	
5	$Ir(PO)(POH)(CO)$	$CDCl_3$	39.84(s)	35.86(s)	132.33(m)	197.39(s)	178(s)	216.51(s)
6	$Ir(PO)_2(POH)(Cl)$	$CDCl_3$	39.34(d) (13.18)	33.18(d) (8.78)	134.49(m)	190.84(s)	175(s)	
7	$Pd(PO)(POH)(Cl)$	DMSO-d_6	39.37(s)	35.85(s)	133.91(m)	203.04(s)	177.89(s)	
8	$Pt(PO)(POH)(Cl)$	DMSO-d_6	39.25(s)	36.38(s)	133.62(m)	185.28(s)	178(s)	

[a] Values are reported in ppm relative to Me_4Sl; values in parentheses are $J(P-H)/J(P-C)$ coupling constants in Hz; ±0.02 ppm; $J \pm 0.2$ Hz. [b] $PO = Ph_2PCH_2COO^-$; $POH = Ph_2PCH_2COOH$. [c] s = singlet; d = doublet; t = triplet; m = multiplets and b = broad.

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