

Synthesis and Characterization of Ru(II) and Ru(III) Complexes of Diphenylphosphinoacetic Acid and their Interaction with Small Molecules

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Abstract

Complexes of Ru(II) and Ru(III) with the bidentate ligand diphenylphosphinoacetic acid (POH) are reported. The ligand POH reacts with $\text{RuCl}_2(\text{PPh}_3)_3$ in a 1:3 ratio to give a five-coordinate complex of composition $\text{Ru}(\text{PO})_2(\text{POH})$ with complete displacement of PPh_3 . In a 1:2 ratio however the complex $\text{Ru}(\text{PO})_2(\text{PPh}_3)$ is formed. The reaction of POH with $\text{RuCl}_2(\text{DMSO})_4$ in a 2:1 ratio afforded a yellow complex of composition $\text{HRu}(\text{PO})_2\text{Cl}(\text{DMSO})$. In a 3:1 ratio of POH to $\text{RuCl}_2(\text{DMSO})_4$ however, the complex $\text{HRu}(\text{PO})_3$ was obtained. Neutral complexes of the composition $\text{Ru}(\text{PO})_2\text{Cl}(\text{AsPh}_3)$ and $\text{Ru}(\text{PO})_3$ were obtained by the reaction of $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}$ with POH in 1:2 and 1:3 mole ratios in acetone solution, respectively. A dimeric chloro bridged complex of composition $[\text{Ru}(\text{PO})_2\text{Cl}]_2$ was obtained on reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with POH in methanol. The complexes have been characterized on the basis of elemental analysis ^1H , ^{13}C - $\{^1\text{H}\}$ and ^{31}P - $\{^1\text{H}\}$ NMR, EPR and electrochemical studies.

The square pyramidal complexes 1 and 2 undergo facile addition reactions with CO , H_2 , PPh_3 and DMSO to form octahedral species. The redox potentials $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ of the complexes become more positive with an increase in the π -acidity of the ligand coordinated to the metal ion.

Introduction

The importance of unsymmetrical bidentate ligands particularly phosphines for selectivity in homogeneous catalysis is illustrated by several recent publications [1–3]. The coordination chemistry of these ligands is therefore of particular interest and is currently being investigated by many research groups including our group.

We have been interested recently in the synthesis [4] and chemistry of transition metal complexes of

unsymmetrical ligands containing mixed donor atoms such as P and N. The ligand (POH) which has the combination of hard and soft donor groups confers the necessary nucleophilicity on the metal ion because of the acetate group whereas the soft donor tertiary phosphine provides π -acidity to stabilize the low valent metal centers [5]. Both the factors are of direct importance to homogeneous catalysis [6, 7]. The unusual combination of hard and soft donor atoms in these ligands leads to interesting structural types and/or reactivity pattern of the complexes towards small molecules.

In this paper we report the synthetic and electrochemistry of Ru(III) and Ru(II) complexes of the ligand diphenylphosphinoacetic acid (POH). The addition reactions of square pyramidal complexes of Ru(II) with CO , H_2 , PPh_3 and DMSO have also been investigated. The reactions represent the facial conversion of five-coordinate complexes to a six-coordinated species.

Experimental

The ligand diphenylphosphinoacetic acid (POH) was synthesized by the published procedure [5]. The complexes $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}$ and $\text{RuCl}_2(\text{Me}_2\text{SO})_4$ [8] were prepared by reported procedures. All organic solvents were distilled under nitrogen and dried prior to use. All reactions were performed in Schlenk-type flasks under nitrogen.

Elemental analyses of C, H, P and Cl were performed by Australian Mineral Development Laboratories (AMDEL), Australia. Melting points, magnetic susceptibility and conductivity measurements were done as reported earlier [9].

Infrared spectra were recorded in the region $4000\text{--}600\text{ cm}^{-1}$ on a Beckman IR-12 spectrophotometer as KBr pellets. Far-infrared spectra ($600\text{--}100\text{ cm}^{-1}$, in Nujol mulls pressed between polyethylene films) were recorded on a Nicolet 200 SXV FT-IR spectrometer.

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The ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 99.55, 40.27 and 24.99 MHz, respectively on a Jeol FX100 FT-NMR, in the indicated solvents. Proton and carbon chemical shifts are positive downfield relative to external tetramethylsilane. Positive phosphorous chemical shifts indicate a downfield position relative to 85% H_3PO_4 . ESR measurements were made with a Bruker-ESP 300 X-band spectrometer. The components of the g tensor were measured relative to diphenylpicrylhydrazyl (DPPH) ($g = 2.0036 \pm 0.0003$).

Electrochemical measurements (cyclic voltammetry and differential pulse polarography) were carried out with the help of a PAR 174 Polarographic analyzer, PAR 175 Universal Programmer, PAR RE 0089 X-Y recorder, PAR 173 Potentiostat, PAR 303 SMDE and PAR 377 A Cell systems. The three electrode measurements were carried out with the use of planar BAS model PTE platinum inlay working electrode; a platinum wire auxiliary electrode and a Ag/AgCl reference electrode. The end of the reference electrode bridge tube filled with saturated KCl solution, was fused to a fine capillary so as to have good electrical contact with minimum diffusion of water and foreign ions into the experimental solution. The experimental results were obtained on a platinum working electrode (area 0.012 cm^2) in CH_3CN or DMF containing 0.1 mol dm^{-3} tetrabutyl ammonium perchlorate under nitrogen atmosphere. The data were obtained at 298 K and are uncorrected for junction potentials. The potentials $E_{1/2}$ for reversible and irreversible electrode reaction were measured as the $0.5 (E_{pa} + E_{pc})$ and peak potentials of differential pulse polarogram recorded with 50 mV amplitude and 10 mV/s scan speed, respectively.

Microanalytical data, conductivity, melting point and magnetic susceptibility data are presented in Table I. The $^{31}\text{P}\{^1\text{H}\}$ NMR data are presented in Table II. The $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR data are presented in Table III.

Synthesis of the Complexes

Bis(diphenylphosphinoacetato)diphenylphosphinoacetic acid ruthenium(II), Ru(PO)₂(POH)(1)

The complex $\text{RuCl}_2(\text{PPh}_3)_3$ (0.200 g, 0.208 mmol) was dissolved in 25 ml of acetone. To this solution 0.153 g (0.627 mmol) of diphenylphosphinoacetic acid (POH) was added and the solution refluxed for 2 h during which period the colour of the solution changed from dark brown to bright yellow. The yellow crystals that separated out were filtered off, washed with acetone and recrystallized from methanol. Yield 60%.

Triphenylphosphinebis(diphenylphosphinoacetato)ruthenium(II), Ru(PO)₂PPh₃(2)

To the brown solution of the complex $\text{RuCl}_2(\text{PPh}_3)_3$ (0.200 g, 0.208 mmol) in acetone (20 ml), an acetone solution of ligand POH (0.102 g, 0.417 mmol) was added. The colour of the solution changed from dark brown to orange yellow. The resulting solution was refluxed for 5 h under N_2 gas. On keeping the reaction mixture overnight at 0°C , orange–yellow crystals separated that were washed with acetone. The complex was recrystallized with dichloromethane–*n*-hexane mixture. Yield 65%.

TABLE I. Analytical, Conductivity and Magnetic Susceptibility Data of Ru(II) and Ru(III) Complexes

| Complex ^a | Colour | Melting point ^b | Conductivity ^c ($\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) | $\mu_{\text{eff}}^{\text{d}}$ (BM) | Elemental analysis (%) ^a | | | |
|---|---------------|----------------------------|--|---------------------------------------|-------------------------------------|----------------|------------------|----------------|
| | | | | | C | H | P | Cl |
| 1 $\text{Ru}(\text{PO})_2\text{POH}$ | yellow | 235–238 | 12 | diamag. | 61.00 (60.64) | 4.46 (4.48) | 11.28 (11.18) | |
| 2 $\text{Ru}(\text{PO})_2\text{PPh}_3$ | orange–yellow | 213–215 | 15 | diamag. | 64.90 (65.01) | 4.59 (4.63) | 11.00 (10.95) | |
| 3 $\text{H}[\text{Ru}(\text{PO})_2(\text{Cl})(\text{Me}_2\text{SO})]$ | pale yellow | 240–243 | 78 | diamag. | 50.90 (51.32) | 4.51 (4.45) | 9.01 (8.83) | 5.02 (5.05) |
| 4 <i>fac</i> - $\text{H}[\text{Ru}(\text{PO})_3]$ | yellow | 290 | 65 | diamag. | 60.20 (60.64) | 4.50 (4.48) | 11.08 (11.18) | |
| 5 $\text{Ru}(\text{PO})_2(\text{Cl})(\text{AsPh}_3)$ | red | 230–232 | 11 | 1.97 | 59.50 (59.45) | 4.18 (4.23) | 6.80 (6.67) | 3.76 (3.82) |
| 6 <i>mer</i> - $[\text{Ru}(\text{PO})_3]$ | dark yellow | 238–240 | 17 | 2.06 | 60.30 (60.72) | 4.26 (4.36) | 11.10 (11.19) | |
| 7 $[\text{Ru}(\text{PO})_2\text{Cl}]_2$ | green | 275–277 | 18 | 3.34 | 52.81 (52.98) | 3.96 (3.88) | 10.20 (9.95) | 5.70 (5.66) |

^aPO = diphenylphosphino acetate; POH = diphenylphosphinoacetic acid. ^bDecomposition temperature. ^cConductivity measured in DMF. ^dBM values are after diamagnetic corrections. ^eCalculated values are in parentheses.

TABLE II. $^3\text{P}\{^1\text{H}\}$ NMR Spectral Data^a of Ru(II) and (III) Complexes

| Complex | Solvent | Spectrum type | Chemical shifts δ (ppm) | | | Coupling constants | | |
|--|--|-----------------|--------------------------------|----------------|----------------|------------------------------|------------------------------|------------------------------|
| | | | P _A | P _B | P _C | $^2J(\text{P}_A-\text{P}_B)$ | $^2J(\text{P}_A-\text{P}_C)$ | $^2J(\text{P}_B-\text{P}_C)$ |
| $\text{Ph}_2\text{PCH}_2\text{COOH}$ | CDCl_3 | A | -15.98(s) | | | | | |
| 1 $\text{Ru}(\text{PO})_2(\text{POH})$ | CH_3OH | ABC | 47.89(t) | 27.13(q) | 27.13(q) | 29.4 | 29.4 | 43.4 |
| 1a $\text{Ru}(\text{PO})_2(\text{POH})(\text{CO})$ | CH_2Cl_2 | ABC | 6.68(t) | 16.43(q) | 16.43(q) | 31.7 | 31.7 | 51.12 |
| 1b $\text{Ru}(\text{PO})_2(\text{POH})(\text{MeOH})$ | CH_3OH | ABC | 36.99(t) | 19.80(q) | 19.80(q) | 23.3 | 23.3 | 37.0 |
| 1c $\text{Ru}(\text{PO})_2(\text{CO})_2$ | CH_3OH | AB | 23.19(d) | 8.57(d) | | 36.00 | | |
| 1e $[\text{Ru}(\text{PO})_2(\text{Me}_2\text{SO})_2]$ | $\text{C}_6\text{H}_5\text{NO}_2$ | AB | 37.69(d) | 33.63(d) | | 31.8 | | |
| 1f $[\text{Ru}(\text{PO})_3]^-$ | CH_2Cl_2 | A | 37.42(s) | | | | | |
| 2 $\text{Ru}(\text{PO})_2\text{PPh}_3$ | CHCl_3 | ABC | 54.43(t) | 41.11(t) | 36.51(t) | 37.00 | 37.00 | 37.00 |
| 2a $[\text{Ru}(\text{PO})_2(\text{PPh}_3)(\text{CO})]$ | CHCl_3 | ABC | 25.30(t) | 43.230(t) | 36.80(t) | 22.00 | 22.00 | 22.00 |
| 3 a) $[\text{Ru}(\text{PO})_2(\text{Me}_2\text{SO})]^-$ | $\text{DMSO}-d_6/\text{CH}_3\text{OH}$ | AB | 40.14(d) | 34.93(d) | | 29.00 | | |
| b) $[\text{Ru}(\text{PO})_2(\text{Cl})(\text{Me}_2\text{SO})]^-$ | $\text{DMSO}-d_6 + \text{CH}_3\text{OH}$ | AB | 37.69(d) | 33.54(d) | | 32.00 | | |
| 4 <i>fac</i> - $[\text{Ru}(\text{PO})_3]^-$ | $\text{DMSO}-d_6$ | A | 37.42(s) | | | | | |
| 5 $\text{Ru}(\text{PO})_2(\text{Cl})(\text{AsPh}_3)$ | $\text{C}_6\text{H}_5\text{NO}_2$ | A | 25.1(s) | | | | | |
| 6 <i>mer</i> - $[\text{Ru}(\text{PO})_3]$ | $\text{C}_6\text{H}_5\text{NO}_2$ | AB ₂ | 32.07(t) | 27.00(d) | | 35.00 | | |

^aChemical shifts in parts per million relative to 85% H_3PO_4 with positive values downfield from the standard; the coupling constants are in Hz; abbreviations: s = singlet, d = doublet, t = triplet, q = quartet.

^b $\text{P} = \text{Ph}_2\text{PCH}_2\text{COO}^-$, $\text{POH} = \text{Ph}_2\text{PCH}_2\text{COOH}$.

Chlorodimethylsulphoxidebis(diphenylphosphinoacetato)ruthenate(II), cis-[Ru(PO)₂(Cl)(Me₂SO)]⁻ (3)

A solution of $\text{RuCl}_2(\text{Me}_2\text{SO})_4$ (0.150 g, 0.309 mmol) in dry ethanol (15 ml) was mixed with POH (0.150 g, 0.618 mmol) and the resulting mixture refluxed for 3 h. The pale yellow crystals obtained were filtered off, washed with warm alcohol and dried *in vacuo*. Yield 75%.

Tris(diphenylphosphinoacetato)ruthenate(II), fac-[Ru(PO)₃]⁻ (4)

The complex $\text{RuCl}_2(\text{Me}_2\text{SO})_4$ (0.150 g, 0.309 mmol) in dry ethanol (15 ml) was mixed with an alcoholic solution of POH (0.240 g, 0.984 mmol). The resulting solution was refluxed until the crystallization of the product commenced. The mixture was allowed to cool to room temperature. The cream coloured crystals were filtered, washed with warm ethanol and recrystallized from dichloromethane. Yield 68%. In an alternate procedure complex 4 was obtained by refluxing complex 1 in THF, in the presence of triphenylphosphine for about 4 h.

Chlorotriphenylarsinebis(diphenylphosphinoacetato)ruthenium(III), trans-[Ru(PO)₂(Cl)(AsPh₃)] (5)

To an acetone solution of the complex $\text{RuCl}_3(\text{AsPh}_3)_3 \cdot \text{MeOH}$ (0.200 g, 0.235 mmol) a solution of the ligand POH in acetone (0.115 g, 0.470 mmol) was added when the colour of the solution changed from green to red. The resulting solution was refluxed for an hour and the red crystalline complex filtered off, washed with acetone and dried *in vacuo*. Yield 65%.

Tris(diphenylphosphinoacetato)ruthenium(III), mer-Ru^{III}(PO)₃ (6)

The complex was prepared according to the procedure for complex 5, by reacting $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}$ and POH in a ratio of 1:3. The green colour of the solution turned from red to yellow on refluxing. The solution was allowed to cool overnight. The yellow crystalline complex that separated out was filtered, washed with acetone and recrystallized from acetonitrile-n-hexane mixture. Yield 55%.

Bis(diphenylacetato)ruthenium(III)- μ -chlorobis(diphenylacetato)ruthenium(III), [Ru(PO)₂-Cl]₂ (7)

To a methanolic solution of ruthenium trichloride (0.200 g, 0.763 mmol) a solution of POH (0.569 g, 2.295 mmol) in methanol was added. The dark brown colour of the solution instantaneously changed to light green. The resulting solution was refluxed for an hour and the green crystalline complex filtered off, washed with methanol and dried *in vacuo*. Yield 75%.

TABLE III. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Data^a of Ru(II) Complexes

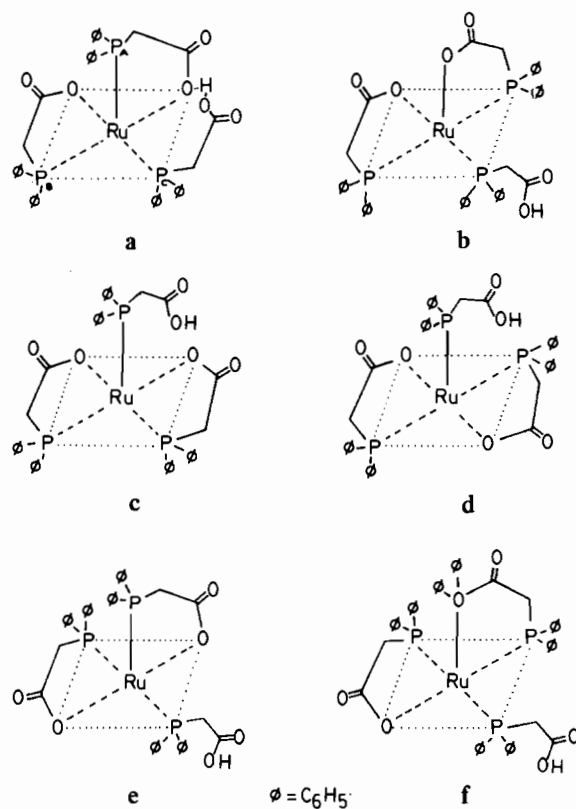
| Complex ^b | Solvent | ^1H Chemical shifts | | | $^{13}\text{C}\{^1\text{H}\}$ Chemical shifts | | | | |
|---|--------------------------|------------------------------|-----------|---------|---|-----------|----------|-----------|-----|
| | | Phenyl | Methylene | | Methyl | Methylene | | Carboxyl | |
| | | | PO | POH | | PO | POH | PO | POH |
| $\text{Ph}_2\text{PCH}_2\text{COOH}$ | CDCl_3 | 7.36(m) | | 3.10(d) | | 35.34(d) | | 177.08(d) | |
| 1 $\text{Ru}(\text{PO})_2\text{POH}$ | CD_3OD | 7.98(m) | 3.61(b) | 3.4(d) | | 39.49(d) | 36.96(d) | 198.32(d) | |
| 2 $\text{Ru}(\text{PO})_2\text{PPh}_3$ | CDCl_3 | 7.90(m) | 3.70(d) | | | 41.5(b) | | 201.96(d) | |
| | | | 3.62(d) | | | | | 198.08(d) | |
| | | | (8) | | | | | (6) | |
| 3 $[\text{Ru}(\text{PO})_2(\text{Cl})(\text{Me}_2\text{SO})]^-$ | $d_6\text{-DMSO}$ | 8.12(m) | 3.86(d) | 3.46(d) | 39.89(d) | | | 187.81(s) | |
| | | | (4) | (5) | (11) | | | 186.70(s) | |
| | | | 3.81(d) | | | | | | |
| | | | (5) | | | | | | |
| | | | 3.76(d) | | | | | | |
| | | | (8) | | | | | | |
| 4 $[\text{Ru}(\text{PO})_3]^-$ | CD_2Cl_2 | 8.05(m) | 3.75(d) | | 40.04(d) | | | 190.01(d) | |
| | | | (10) | | (8.18) | | | (9.6) | |

^aChemical shifts in parts per million relative to Me_4SO ; values in parentheses are $J(\text{P-H})/J(\text{P-C})$ in Hertz; $\delta \pm 0.2$ Hz; abbreviations: s = singlet, d = doublet, b = broad. ^bPO = diphenylphosphinoacetate; POH = diphenylphosphinoacetic acid.

Results and Discussion

The reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ and POH in a 1:3 molar ratio under reflux in acetone gave a diamagnetic Ru(II) complex of composition $\text{Ru}(\text{PO})_2(\text{POH})$ (1). Complex 1 is a non-electrolyte as shown by its conductivity value in MeOH and DMF solutions [10] (Table I). The far-infrared spectrum of 1 shows no bands in the metal chloride spectral region suggesting the displacement of all the chlorides by POH in 1. The presence of two strong bands at 1690 and 1580 cm^{-1} are indicative of $\nu(\text{COOH})$ free and $\nu(\text{COO}^-)$ chelated carboxyl groups, respectively [11].

The analytical and spectroscopic data of 1 are in accord with five-coordinated ruthenium(II) species, which is likely to have a square pyramidal geometry as favoured theoretically [12] and by analogy of the complexes $\text{RuCl}_2(\text{PPh}_3)_3$ [13, 14] $[\text{Ru}(\text{H})(\text{Cl})(\text{PPh}_3)_3]$ [15], $[\text{RuXL}_4]$ [16] and $[\text{RuCl}(\text{diphosphine})_2]^+$ [17]. For the latter complex McAullife *et al.* [18] had reported a trigonal bipyramidal geometry. In complex 1 the $^{31}\text{P}\{^1\text{H}\}$ NMR data are not helpful in assigning either a square pyramidal or trigonal bipyramidal geometry, since both would give an AB_2 or ABC pattern. However, a square pyramidal geometry appears more reasonable for the complex. This is supported by the observed diamagnetism of the complex and the facile addition of a neutral ligand in the sixth-coordinated position to form octahedral complexes.



Scheme 1.

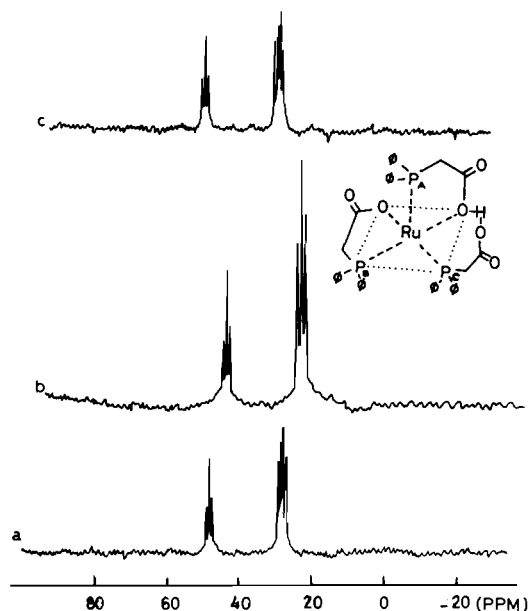


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{Ru}(\text{PO})_2(\text{POH})$: (a) at 300 K in CH_3OH , (b) at 208 K in CH_2Cl_2 , (c) at 373 K in nitrobenzene.

Because of the ambidentate nature of the ligand POH, six isomers are possible for complex **1** (Scheme 1). Of these, two isomers have one monodentate POH on an apical position and four isomers on basal positions. In the former case ^{31}P NMR spectrum would give an AB_2 pattern whereas in the latter case it would give an ABC type of spectrum. The ^{31}P NMR spectrum of **1** consists of an ABC pattern (Fig. 1a) with a triplet centered at 47.89 ppm and a quartet centered at 27.13 ppm with the integrated intensity ratio of 1:2. The $^2J(\text{P}_\text{A}-\text{P}_\text{B})$ and $^2J(\text{P}_\text{A}-\text{P}_\text{C}) = 29.4$ Hz and $^2J(\text{P}_\text{B}-\text{P}_\text{C}) = 43.4$ Hz, respectively (Table II). The $J(\text{P}-\text{P})$ values are in agreement with those previously reported for non-equivalent phosphorous atoms *cis* to one another in Ru(II) tertiary phosphine complexes [19]. A value about ten times larger is expected for *trans* $J(\text{P}-\text{P})$ coupling [19–21]. The observed ABC pattern of the ^{31}P spectrum rules out the possibility of isomers a, b and d on the basis of the magnitude of $^2J(\text{P}-\text{P})$ values. The isomers e and f can also be ruled out since in this case one would have expected large coupling constants for non-equivalent *trans* phosphorous atoms thus leaving the possibility of only the isomer c as the possible structure of **1**. The triplet and quartet with a 1:2 intensity for an ABC pattern is quite surprising. The pattern of resonance and the relative intensities of the peaks does however suggest [1] that even though three phosphorous atoms are magnetically non-equivalent, yet the resonances of P_B and P_C exactly overlap to give a quartet because of their *trans* configuration to oxygen. On the grounds of ring contribution factor (ΔR) one would have expected

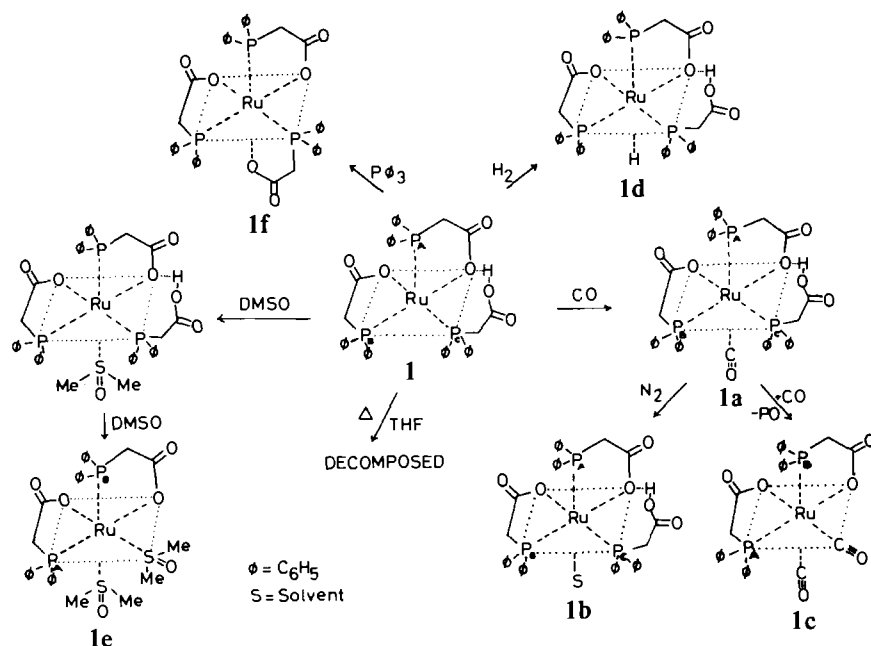
a quartet at low field for P_B , which is deshielded to the extent of 24 ppm [22] when compared to pseudochelate intermolecular hydrogen bonded P_C phosphorous atom. But the observed spectrum shows overlapping resonance of P_B and P_C phosphorous. There is no change in the ^{31}P NMR spectrum even at 373 K in nitrobenzene (Fig. 1c), however, there is change at 208 K in MeOH and CD_2Cl_2 (Fig. 1b). The low temperature spectrum shows two triplets at 46.00 and 25.43 ppm with a 1:2 intensity ratio (Fig. 1b), with $^2J(\text{P}-\text{P})$ equal to 26.9 Hz. The large downfield resonance of apical phosphorous (P_A) is due to the absence of a competing *trans* ligand for electron density along the z-axis on the metal ion which suggests that the square pyramidal structure is maintained as it is characterized by widely different bond lengths $\text{Ru}-\text{P}_\text{basal} > \text{Ru}-\text{P}_\text{apical}$ [14, 15].

The proton NMR spectrum of **1** in CD_3OD shows a broad peak at 3.61 ppm due to methylene protons. The absence of any peak at 2.2 ppm rule out the possibility of solvation (acetone) of complex **1**. The proton and $^{13}\text{C}\{^1\text{H}\}$ NMR data of **1** are tabulated in Table III.

Reaction of **1** with CO

When CO was bubbled through the methanolic solution of **1** at 300 K a light yellow complex was obtained (Scheme 2). The disappearance of **1** was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR and IR spectroscopy. The IR spectrum of **1a** shows a single sharp band at 2035 cm^{-1} due to $\nu(\text{Ru}-\text{CO})$ which is in the range noted for CO *trans* to phosphorous [23].

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the carbonyl complex **1a** shows a triplet centered at 6.68 ppm and a quartet centered at 16.43 ppm with $^2J(\text{P}_\text{A}-\text{P}_\text{B}) = 31.7$; $^2J(\text{P}_\text{A}-\text{P}_\text{C}) = 31.7$ Hz and $^2J(\text{P}_\text{B}-\text{P}_\text{C}) = 51.12$ Hz (Fig. 2). The high field triplet can be assigned to the P_A phosphorous atom which is *trans* to the strong π -acidic ligand CO. The difference in P_A and P_B resonances in complexes **1** and **1a** is expected since the geometry of the complex **1** changes from a square pyramid to an octahedral one in **1a**. The significant feature of this reaction is the addition of a π -acid ligand CO to a low valent transition metal complex. The reaction is readily reversible on purging N_2 gas in the methanol solution of **1a**. After CO elimination complex **1a** is not reverted back to **1**, instead it gave **1b** with MeOH coordination in the sixth position. The ^{31}P NMR spectrum **1b** (Fig. 2) shows a triplet centered at 36.99 ppm and a quartet centered at 19.80 ppm. On prolonged passing of CO for 6 h through a methanolic solution of **1** the dicarbonyl species **1c** was obtained. The ^{31}P NMR spectrum of **1c** shows two doublets centered at 23.19 and 8.57 ppm ($^2J(\text{P}-\text{P}) = 36$ Hz) and a peak at -16.35 ppm. The IR spectrum of **1c** shows two $\nu(\text{CO})$ bands at 2012 and 1978 cm^{-1} suggesting a



Scheme 2.

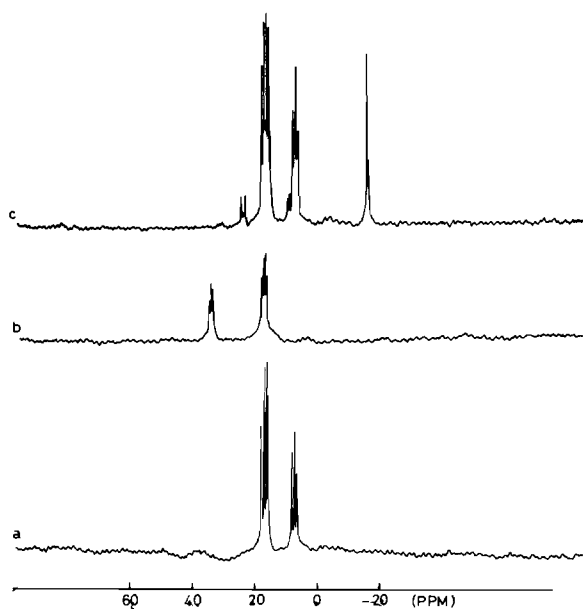


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{Ru}(\text{PO})_2(\text{POH})$ in CH_3OH : (a) at 300 K after bubbling CO gas for 40 min, (b) after purging N_2 gas in the above carbonylated complex **1a**, (c) after passing CO gas for 6 h in complex **1**.

cis geometry of the two carbonyls. The ^{31}P NMR coupled with IR data unambiguously suggest that a monodentate phosphine is replaced by CO on prolonged passing of CO (Fig. 2c).

Reaction of **1** with H_2

The methanolic solution of complex **1** reacts with hydrogen at 30°C to give an exclusive monohydrido species **1d**. The product was characterized by a ^1H NMR spectrum. The ^1H NMR spectrum of **1d** shows two triplets centered at -16.61 and 18.13 ppm ($J(\text{P}-\text{H})(\text{trans}) = 151$ Hz, $J(\text{P}-\text{H})(\text{cis}) = 23$ Hz). The IR spectrum shows a broad band at 1790 cm^{-1} due to $\nu(\text{Ru}-\text{H})$.

Reaction of **1** with Me_2SO

By adding 4% (by volume) Me_2SO solvent to the nitro-benzene solution of **1**, the $^{31}\text{P}\{^1\text{H}\}$ resonance signals attributed to **1** disappeared slowly as the reaction with Me_2SO proceeds. New resonances appear at 37.69 , 33.63 (doublets $J(\text{P}-\text{P}) = 31.8$ Hz) and -17.25 ppm assigned to two bidentate P_A and P_B phosphorous atoms and uncoordinated phosphorous nuclei (Fig. 3), suggesting *in situ* formation of **1e**. The IR spectrum of **1e** shows strong bands at 1096 and 1102 cm^{-1} due to $\nu(\text{S}=\text{O})$ (stretching frequency of the S-bonded *cis* Me_2SO groups) [8].

Reaction of **1** with Triphenyl Phosphine

Complex **1** in the presence of PPh_3 in MeOH on prolonged heating is converted to a more stable complex **1f**. The ^{31}P NMR spectrum of the product shows a singlet at 37.42 ppm indicating a structural rearrangement of complex **1** to give the *fac* isomer **1f**. This suggests an initial coordination of PPh_3 to the sixth position in the square pyramidal complex **1** which is later displaced by the free carboxylate arm

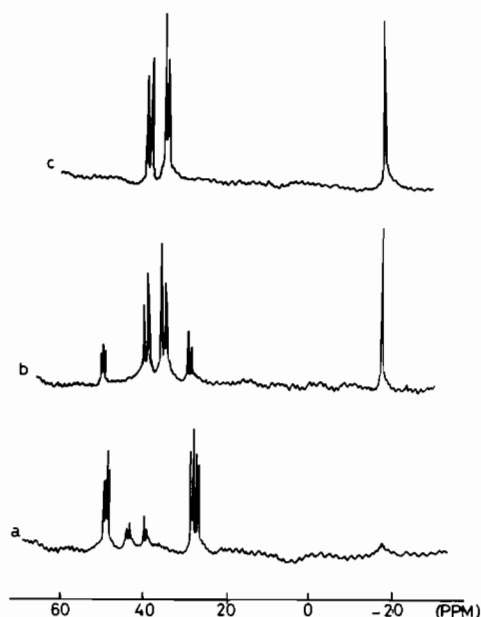


Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Ru}(\text{PO})_2(\text{POH})$ in nitrobenzene: (a) 20 min after adding Me_2SO (4% by volume), (b) 2 h after adding Me_2SO , (c) 4 h after adding Me_2SO .

of the POH ligand to form an octahedral complex. Attempts to identify the intermediate PPh_3 coordinated complex at 300 K by ^{31}P NMR failed. This may be due to steric crowding of the phenyl group of PPh_3 which is readily displaced by a free carboxylate group in a fast step.

Complex **2** is a non-electrolyte and diamagnetic (Table I). The infrared spectrum of **2** shows a strong broad band at 1600 cm^{-1} due to coordinated $\nu(\text{COO}^-)$ carboxylate. The far-IR spectrum of **2** shows bands at 510, 502 and a shoulder at 495 cm^{-1} due to $\nu(\text{Ru}-\text{P})$ of PO and PPh_3 , respectively. Complex **2** is a five-coordinate species as supported by its analytical and spectroscopic data. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** shows an ABC pattern with three well resolved triplets centered at 54.43, 41.11 and 36.51 ppm (Fig. 4) ($^2J(\text{P}-\text{P}) = 37\text{ Hz}$). The observed ^{31}P pattern and coupling constants unambiguously suggest that the three phosphorous atoms are in facial arrangements. The triplet centered at 54.43 ppm can be assigned to the apical (P_A) phosphorous atom. This assignment is suggested on the grounds that a large coordination chemical shift $\Delta((\text{complex}) - (\text{free ligand}))$ is expected for the apical phosphine, which is closer to metal ion than the basal phosphorous atoms [14, 15]. The remaining two triplets centered at 41.11 and 36.51 ppm are assigned to P_B and P_C phosphorous atoms, respectively.

The proton decoupled $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** shows two doublets centered at 201.96 and 198.08 ppm with $^2J(\text{P}-\text{C}) = 6\text{ Hz}$ assigned to coordinated

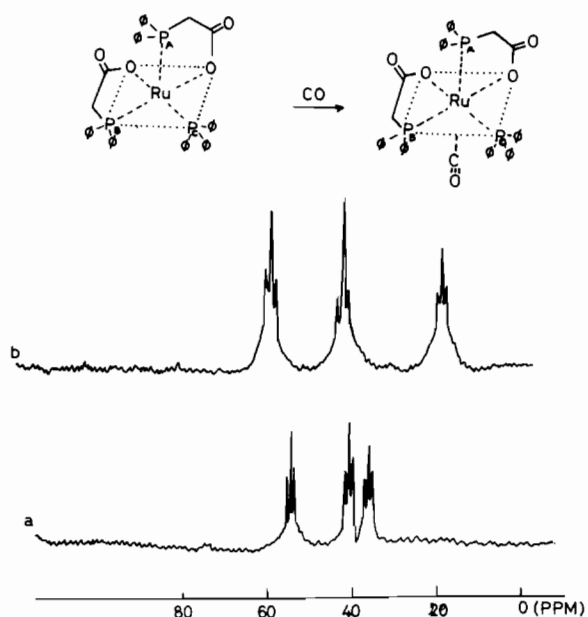


Fig. 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of: (a) $\text{Ru}(\text{PO})_2\text{PPh}_3$ in CHCl_3 , (b) **2** after passing CO gas for 40 min.

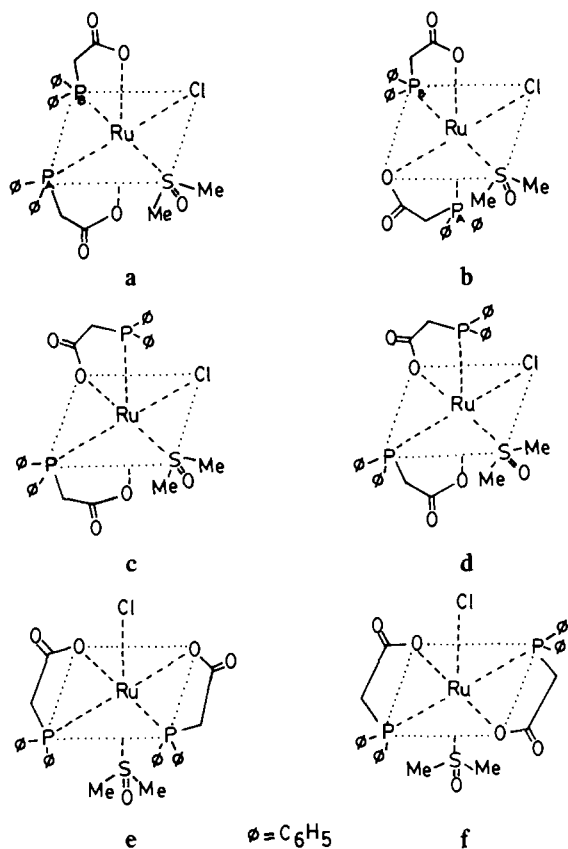
carboxylate groups. The peaks corresponding to aliphatic and aromatic region are tabulated in Table III. The proton NMR spectrum of **2** shows two doublets centered at 3.62 and 3.70 ppm ($^2J(\text{P}-\text{H}) = 8\text{ Hz}$) assigned to $\text{P}-\text{CH}_2$ protons, a pattern frequently observed when two PPh_2CH_3 or PPh_2CH_2 units are in *cis* positions [24, 25].

Reaction of **2** with CO

Reaction of a solution of **2** with CO results in a rapid conversion of **2** to a greenish yellow carbonylated species **2a**. The disappearance of **2** on carbonylation is easily followed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Table II). The ^{31}P NMR spectrum of **2a** shows three triplets centered at 25.30, 43.2 and 36.8 ppm with $^2J(\text{P}-\text{P}) = 22\text{ Hz}$ assigned to P_A , P_B and P_C phosphorous atoms, respectively (Fig. 4b). The high field shift of the P_A phosphorous atom from 54.43 to 25.30 ppm on going from **2** to **2a** is due to the *trans* effect of the CO ligand in **2b**. The IR spectrum of **2a** shows a strong peak at 2049 cm^{-1} due to $\nu(\text{Ru}-\text{CO})$ [8].

Reaction of **2** with H_2

Purging of H_2 through the solution of **2** gave a hydrido species **2b** which was characterized by ^1H NMR. The ^1H NMR of **2b** shows a doublet of doublets centered at -24.56 ppm . The four doublets can be explained on the basis of the fact that the resonance signal due to the hydride is split by the *trans* phosphorous (P_A) nucleus into a doublet ($^2J(\text{P}-\text{H}) = 165\text{ Hz}$) and then split by two non-



Scheme 3.

equivalent phosphorous atoms P_B and P_C , respectively ($^2J(P_B-H) = 28.93$ Hz; $^2J(P_A-H) = 18.6$ Hz). The large coupling constant suggests that the hydride is *trans* to the (P_A) phosphorous atom. The high field resonance of the hydride indicates the extent of antishielding of the metal nucleus. The chemical shifts and coupling constants are in close agreement with the earlier reports [26].

Electrochemistry of Complexes 1 and 2 and their Respective Carbonyls

Complex 1 and 2 provide an opportunity to observe the effect of the displacement of chlorides by carboxylates, on the relative ease of metal oxidation. Complexes 1 and 2 undergo a reversible one electron oxidation at $E_{1/2} + 0.43$ and $+0.58$ V, respectively, *versus* SCE, under a nitrogen atmosphere. Comparison of the oxidation potentials of the related complex $RuCl_2(PPh_3)_3$ [27] under similar conditions ($E_{1/2} = 0.76$ V) shows the shifts of the potentials to more negative values on substitution of chlorides by a basic carboxylate group of the bidentate PO.

When CO was bubbled through the solution of 1 and 2 its oxidation peaks disappear within a few minutes and new peaks appear corresponding to

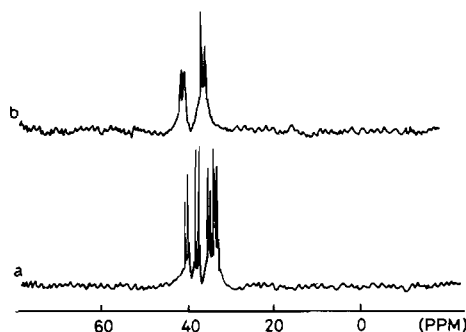
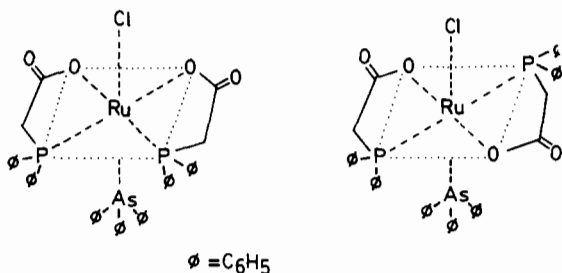


Fig. 5. $^{31}P\{^1H\}$ NMR spectra of $[Ru(PO)_2Cl(Me_2SO)]^-$ in $Me_2SO/MeOH$ mixed solvent: (a) at 300 K, (b) at 220 K.

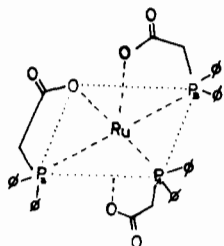
the potentials $E_{1/2} = +0.9$ V and $+1.13$ V, (reversible oxidation) for complexes 1a and 2a, respectively. The more positive $E_{1/2}$ values obtained for 1a and 2a as compared to those of 1 and 2 are in agreement with decreasing electron density on the Ru(II) upon coordination of a strong π -acidic ligand CO.

Displacement reaction of coordinated Me_2SO in the complex $RuCl_2(Me_2SO)_4$ with POH in a 1:2 molar ratio, under reflux ethanol, gave a pale yellow crystalline anionic complex of composition $[Ru(Cl)(PO)_2(Me_2SO)]^-$ (3). In the reaction of $RuCl_2(Me_2SO)_4$ with POH the weakly coordinated O-bonded Me_2SO groups are displaced first, leaving the S-bonded Me_2SO group coordinated to the metal ion. The IR spectrum of 3 shows a strong sharp band at 1578 cm^{-1} which is assigned to coordinated $\nu(COO)$ of the carboxylate group. A sharp band at 1086 cm^{-1} $\nu(S=O)$ suggests the presence of an S-bonded Me_2SO group. The far-infrared spectrum of 3 shows absorption bands at 330, 447 and 503 cm^{-1} assigned to $\nu(Ru-Cl)$, $\nu(Ru-S)$ and $\nu(Ru-P)$, respectively. The conductivity of 3 in DMF shows that it is a 1:1 electrolyte(II).

Because of the ambidentate nature of the ligand POH, six geometrical isomers are theoretically possible for complex 3. Four of these isomers have a *cis* disposition of Cl and Me_2SO and two isomers with *trans* Cl and Me_2SO groups. The $^{31}P\{^1H\}$ NMR spectrum of 3 is consistent with the existence of two isomers a and b in a 1:1 ratio in solution (Scheme 3). The $^{31}P\{^1H\}$ NMR of 3 (Table III) (Fig. 5) that displays four doublets centered at 40.14 and 34.39 ppm with $^2J(P-P) = 29$ Hz can be assigned to the phosphorous atoms P_A and P_B of isomer a, respectively. The other two doublets centered at 37.69 and 33.54 ppm with $^2J(P-P) = 32$ Hz are assigned to P_A and P_B phosphorous atoms of isomer b, respectively. It is interesting to note that P_B phosphorous atoms are *trans* to Me_2SO in both the isomers and the relative chemical shifts for P_B are very close, 34.93 and 33.54 ppm in isomers a and b, respectively. Attempts to isolate the isomers at room temperature failed. At low temperature (220 K)



Scheme 4.



Scheme 5.

in methanol isomer **a** is completely converted to **b** (Fig. 5), (doublets centered at 38.94 and 33.89 ppm).

The proton NMR spectrum of **3** (Table III) shows three doublets centered at 3.86 ($^2J(\text{P-H}) = 4$ Hz), 3.18 ($^2J(\text{P-H}) = 5$ Hz) and 3.76 ppm ($J(\text{P-H}) = 9$ Hz) due to PCH_2 protons in isomers **a** and **b**. The doublet at 3.46 ppm ($^2J(\text{PH}) = 5$ Hz) is assigned to the methyl proton of the S-bonded Me_2SO group. The splitting of the methyl proton resonance into a doublet may be due to interaction of the *trans* phosphorous nucleus. There is a considerable downfield shift (≈ 0.70 ppm) in the methylene and phenyl proton resonances as compared to that of the free ligand due to deshielding upon coordination of the metal ion through phosphorous and carboxylate oxygen. The proton decoupled ^{13}C NMR spectrum of **3** shows two peaks at 187.81 and 186.7 ppm suggesting that the phosphorous coupling may be very small and lower than the base line width. The aliphatic ^{13}C NMR data are given in Table III.

Complex **4** was obtained by the displacement of all the coordinated ligands from $\text{RuCl}_2(\text{Me}_2\text{SO})_4$ with the POH ligand. This complex was also obtained from **1**, upon refluxing **1** in MeOH in the presence of PPh_3 . The conductivity, micro-analytical and spectroscopic data of **4** is in accord with the formation of the complex as a facial $\text{Ru}(\text{PO})_3^-$ isomer. In the facial geometry, complex **4** possesses a C_3 axis of symmetry and all the three phosphorous atoms are *trans* to oxygen and are magnetically equivalent. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** (Table II) is in conformity with the proposed geometry and gives a single resonance peak at 37.42 ppm.

Complexes **3** and **4** undergo reversible one electron oxidation at $E_{1/2}$ values of +0.253 and +0.406 V versus SCE, respectively. A solution of the complex $\text{RuCl}_2(\text{Me}_2\text{SO})_4$ in acetonitrile exhibits a one electron reversible redox peak at 0.177 V. The potentials of the Ru(III)/(II) couple of **3** and **4** are more negative than **1** and **2** which suggests that the oxidation of the central metal ion becomes more difficult as the number of π -acidic ligands increase in the coordination sphere of the metal ion.

The reaction of $\text{RuCl}_2(\text{AsPh}_3)_3 \cdot \text{MeOH}$ with POH in a 1:2 molar ratio under reflux in benzene gave complex **5**. The conductivity of **5** in acetonitrile and DMF corresponds to the complex being a non-electrolyte. The μ_{eff} of **5** calculated from the magnetic susceptibility data is 1.97 BM, corresponding to one unpaired electron as expected for low spin ruthenium(III) complexes. The infrared spectrum of **5** exhibits a strong absorption band $\nu(\text{COO})$ at 1606 cm^{-1} . The far infrared spectrum of **5** shows a band at 285 cm^{-1} attributed to $\nu(\text{Ru-Cl})$ in agreement with Ru-Cl frequencies reported earlier for complexes where Cl is *trans* to a triphenylarsine group [23]. The absorption bands at 478, 503 and 511 cm^{-1} are assigned to $\nu(\text{Ru-As})$ and $\nu(\text{Ru-P})$, respectively. The two bands at 503 and 511 cm^{-1} suggest a *cis* agreement of phosphorous atoms in the complex.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** gives a broad resonance peak at 25.10 ppm thereby suggesting that the two phosphorous atoms are magnetically equivalent. The single resonance peak in ^{31}P NMR spectrum could be either for *trans* or *cis* phosphorous atoms as in both cases the two phosphorous atoms are magnetically equivalent. However, the existence of two bands in the $\nu(\text{Ru-P})$ region (503 and 511 cm^{-1}) and on the basis of electronic considerations (strong *trans* director) suggests they are not *trans* to one another [28]. A *cis* geometry has therefore been suggested for the coordinated phosphorous groups (Scheme 4) in **5**. Because of the paramagnetic nature of the complex ^1H NMR could not be of any help in assigning the geometry.

Complex **6** was obtained by the complete displacement of coordinated triphenylarsine and chloride in $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}$ by POH. The μ_{eff} of **6** is 2.06 BM, corresponding to one unpaired electron. The analytical, conductivity and spectroscopic data of **6** unambiguously suggest a meridional configuration of ligands in **6**. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of **6** shows a broad AB_2 spin system, with a triplet and doublet centered at 32.07 and 27.00 ppm, (relative intensities 1:2 ratio) assigned to P_A and P_B phosphorous atoms, respectively ($^2J(\text{P}_\text{A}-\text{P}_\text{B}) = 35$ Hz). It can be seen that the ordering of ^{31}P chemical shifts depends primarily on the ligands *trans* to the phosphorous nucleus, increasing to higher field in the sequence $\text{O} < \text{P}$ (Scheme 5).

Complexes **5** and **6** give reversible one electron reduction of the Ru(III)/(II) couple at $E_{1/2}$ of +0.402 V versus SCE, respectively. The large potential shifts in **5** and **6** towards positive values when compared to the *mer* RuCl₃L₂L' complex (e.g. L = organonitrile, L' = MeOH [29]; L = arsine: L' = pyridine [30]) and RuCl₃(AsPh₃)·MeOH (-0.012 V) is because of the stabilization of the lower valent state of the metal ion in complexes **5** and **6** on PO substitution.

Interaction of POH with RuCl₃ in a 3:1 molar ratio under reflux in methanol give a paramagnetic green complex **7**. The complex was too insoluble for NMR studies and has not been characterized by spectroscopic methods. However, the microanalytical data is in accord with the proposed dimer structure [Ru(PO)₂Cl]₂. Complex **7** is paramagnetic with $\mu_{\text{eff}} = 3.34$ BM corresponding to one unpaired electron per ruthenium centre. The infrared spectrum shows no bands due to free carboxylic acid groups. The far IR spectrum shows two bands at 215 and 230 cm⁻¹ due to bridged chlorides [31].

ESR Spectra

Octahedral low spin d⁵ systems with one unpaired electron give a characteristic ESR signal. The room temperature polycrystalline ESR spectrum of **5** exhibits an anisotropic spectrum with axial distortion and the g values measured are $g_{\parallel} = 1.91$ and $g_{\perp} = 2.37$ with $g_{\text{av}} = 2.14$ [32]. The ESR spectrum of **5** in DMF at 139 K shows rhombic distortion with three g values $g_1 = 2.42$, $g_2 = 2.07$ and $g_3 = 1.69$ (the observed g values are consistent with the reported g values of the complexes of the type RuCl₃L₃ [33] (L = PR₃, AsR₃)). The presence of rhombic distortion is apparent in the splitting of the perpendicular resonance into two spaced components (g_1 and g_2). This is indicative of a gross change in the geometry of the complex in solution. No hyperfine interaction was observed due to the ruthenium nucleus with nuclear magnetic spin $I = 3/2$ and $5/2$.

The ESR spectrum of **6** at room temperature exhibits an anisotropic spectrum which is axial in nature ($g_{\parallel} = 1.97$ and $g_{\perp} = 2.33$) and it does not exhibit any appreciable change in g values ($g_{\parallel} = 1.94$ and $g_{\perp} = 2.31$) in DMF at 139 K [34].

The ESR spectrum of **7** in the polycrystalline state at room temperature exhibits rhombic distortion with three g values at $g_1 = 2.51$, $g_2 = 2.26$ and $g_3 = 1.87$. The observed g values are in close agreement with the reported values [33, 35]. The peak at low field side ($g = 2.51$) is more intense than the peaks at higher field side. This pattern of the ESR spectrum was attributed to the compressed rhombic distortion (reverse rhombic) in the complex [36].

The Ru^{III}/Ru^{II} redox potentials for various ruthenium complexes studied are presented in Table

TABLE IV. Redox Potentials for Ru^{III}/Ru^{II} Couple in the Series of Ruthenium Complexes with Different π -Acidic Ligand Groups

| Complex | Redox potentials $E_{1/2}$ (V) |
|---|--------------------------------|
| Ru(PO) ₂ (PPh ₃)(CO) (2a) | +1.13 |
| Ru(PO) ₂ (POH)(CO) (1a) | +0.97 |
| RuCl ₂ (PPh ₃) ₃ | +0.76 |
| Ru(PO) ₂ (PPh ₃) (2) | +0.58 |
| Ru(PO) ₂ (POH) (1) | +0.43 |
| Ru(PO) ₃ ⁻ (4) | +0.406 |
| Ru(PO) ₃ (6) | +0.406 |
| Ru(PO) ₂ (Cl)(AsPh ₃) (5) | +0.278 |
| Ru(PO) ₂ Cl(Me ₂ SO) (3) | +0.253 |
| RuCl ₂ (Me ₂ SO) ₄ | +0.177 |

IV. The Ru^{III}/Ru^{II} redox potentials depend on the π -acidity of the ligands coordinated to the metal ion and exhibit an interesting trend. As the π -acidity increases the Ru^{III}/Ru^{II} couple shifts to more positive values. This is due to stabilization of the lower valent state of the metal ion (Ru²⁺) with an increase in the π -acidity of the ligand. Based on the Ru^{III}/Ru^{II} potentials, the π -acidity of the ligands decreases in the order CO > PPh₃ > POH > PO > AsPh₃ > DMSO ~ Cl.

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