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Octahedral Complexes of Ruthenium(II) with some Fluorine Substituted Ditertiary Phosphines

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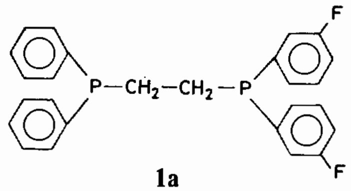
Abstract

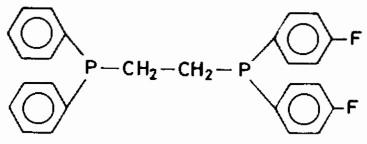
The ditertiary phosphines, 1-diphenylphosphino-2-bis(*m*-fluorophenyl) phosphinoethane (**1a**), 1-diphenylphosphino-2-bis(*p*-fluorophenyl) phosphinoethane (**1b**), 1-diphenylphosphino-2-bis(*m*-trifluoromethylphenyl) phosphinoethane (**1c**) complexes of ruthenium(II) of the type $[Ru(P–P')_2X_2]$ (X = Cl, Br, I, NCS, P–P' = **1a**, **1b** or **1c**) and $[Ru(CO)_2(P–P')X_2]$ (X = Cl, Br, I) have been prepared and characterized on the basis of elemental analysis, IR, UV, ^{1}H NMR and ^{31}P NMR (in a few cases) data. Based on the result of these studies, *trans*- and *cis*-octahedral structures for $[Ru(P–P')_2X_2]$ and $[Ru(CO)_2(P–P')X_2]$ complexes, respectively, have been proposed. In all these cases, the ditertiary phosphines act as potential bidentate chelating ligands.

Introduction

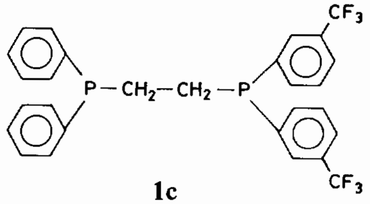
The tertiary phosphine complexes of ruthenium have occupied a unique position in the field of catalysis since the discovery of $[RuHCl(PPh_3)_3]$ which was reported to be an efficient and active hydrogenation catalyst [1]. Tremendous efforts have been made to prepare a variety of monotertiary as well as ditertiary phosphine complexes of ruthenium in order to explore their catalytic behaviour [2–5]. A survey of the literature reveals that although numerous complexes of ruthenium with symmetrical ditertiary phosphines have been extensively studied [6–13], the chemistry of unsymmetrical ditertiary phosphines remained recessive [5]. Studies of the unsymmetrical ditertiary phosphine complexes are much more informative in comparison to the symmetrical analogues since the ^{31}P NMR spectra of the former can provide the direct measurement of phosphorus–phosphorus couplings, ^2J (PMP). Further, the introduction of fluorine into the phenyl ring is expected to increase the solubility characteristic of the resulting complexes, thereby, facilitating the ^{31}P NMR studies. In this paper, we report the syntheses and characterization of eighteen complexes of three new fluorine substituted unsymmetrical ditertiary phosphines (**1a**–**1c**) [16], thereby, substantially expanding our earlier studies [9].



1a



1b



1c

Experimental

Physical measurements and experimental techniques were carried out as described elsewhere [9, 14–16]. Ruthenium trichloride trihydrate was obtained from Johnson and Matthey Ltd., U.K. Dichlorotetrakis(dimethylsulphoxide)ruthenium(II), $[RuCl_2(DMSO)_4]$ [17] and dichlorodicarbonylruthenium(II), $[Ru(CO)_2Cl_2]$ [18] were prepared by reported methods.

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Preparation of Complexes

Dichlorobis{1-diphenylphosphino-2-bis(m-fluorophenyl)phosphinoethane}ruthenium(II), [Ru(1a)$_2$Cl$_2$]

[RuCl$_2$(DMSO)$_4$] (0.42 g, 0.87 mmol) and ligand **1a** (0.76 g, 1.75 mmol) were refluxed in 60 ml of ethanol for 6 h. The yellow solution so obtained was cooled to room temperature and the solvent was removed under vacuum to give a yellow powder. It was recrystallized from a mixture of chloroform and ethanol to yield a microcrystalline yellow solid. Yield 0.81 g, 90%.

Dibromobis{1-diphenylphosphino-2-bis(m-fluorophenyl)phosphinoethane}ruthenium(II), [Ru(1a)$_2$Br$_2$]

[Ru(**1a**)$_2$Cl$_2$] (0.35 g, 0.34 mmol) was refluxed with KBr (20 fold excess) in 50 ml of ethanol for 35 h. After cooling the reaction mixture, the solvent was removed under reduced pressure. The residue was washed with water and the complex was extracted with chloroform. It was finally dried under vacuum to give a yellow powder. Yield 0.23 g, 60%.

Diiodobis{1-diphenylphosphino-2-bis(m-fluorophenyl)phosphinoethane}ruthenium(II), [Ru(1a)$_2$I$_2$]

[Ru(**1a**)$_2$Cl$_2$] (0.28 g, 0.27 mmol) was refluxed with KI (20 fold excess) in 45 ml of ethanol for about 40 h. The complex was extracted as described above. Yield 0.16 g, 50%.

Dithiocyanatobis{1-diphenylphosphino-2-bis(m-fluorophenyl)phosphinoethane}ruthenium(II), [Ru(1a)$_2$(NCS)$_2$]

[Ru(**1a**)$_2$Cl$_2$] (0.25 g, 0.24 mmol) was refluxed with KSCN (20 fold excess) in 35 ml of ethanol for 42 h. The solvent was removed under reduced pressure and the complex was extracted with chloroform to give a cream coloured powder. Yield 0.17 g, 65%.

Dichlorodicarbonyl-1-diphenylphosphino-2-bis-(m-fluorophenyl)phosphinoethane ruthenium(II), [Ru(CO)$_2$(1a)Cl$_2$]

To a nitrogen purged refluxing solution of [Ru(CO)$_2$Cl$_2$] (0.46 g, 2.02 mmol) in 30 ml ethanol, ligand **1a** (0.87 g, 2.00 mmol) was added and the contents were refluxed for 4 h to give a yellow precipitate. It was washed with petroleum ether and dried under vacuum to give a yellow crystalline solid. Yield 0.80 g, 60%.

Dibromo-di-carbonyl-1-diphenylphosphino-2-bis-(m-fluorophenyl)phosphinoethane ruthenium(II), [Ru(CO)$_2$(1a)Br$_2$]

[Ru(CO)$_2$(**1a**)Cl$_2$] (0.26 g, 0.39 mmol) was heated under reflux in 2-methoxyethanol (50 ml) with KBr for 30 h. The reaction mixture was cooled to room temperature and the solvent was removed under vacuum. The residue was washed with water and finally with methanol to give a yellow powder. Yield 0.19 g, 65%.

Di-iododicarbonyl-1-diphenylphosphino-2-bis(m-fluorophenyl)phosphinoethane ruthenium(II), [Ru(CO)$_2$(1a)I$_2$]

[Ru(CO)$_2$(**1a**)Cl$_2$] (0.32 g, 0.48 mmol) was refluxed in 2-methoxy ethanol (40 ml) with KI (10 fold excess) for 30 h. The complex was worked out as described above. Yield 0.22 g, 55%.

Analogous complexes of ligands **1b** and **1c** were prepared by the same methods as described above for ligand **1a**.

Results and Discussion

The reaction of 1-diphenylphosphino-2-bis(*m*- or *p*-fluorophenyl)phosphinoethane and 1-diphenylphosphino-2-bis(*m*-trifluoromethylphenyl)phosphinoethane with [RuCl$_2$(DMSO)$_4$] in ethanol solution yielded complexes of the type *trans*-[Ru(P–P')$_2$Cl$_2$] by complete replacement of the coordinated DMSO groups by the ligand. The complexes of the type [Ru(CO)$_2$(P–P')Cl$_2$] were obtained by the reaction of [Ru(CO)$_2$Cl$_2$] with the corresponding ditertiary phosphine in ethanol. The bromo, iodo and thiocyanato complexes were obtained by metathetical exchange reactions with the corresponding potassium or ammonium salt as described above. Table I enlists the analytical data and some of the physical characteristics of these complexes. Spectroscopic data are given in Table II.

A comparison of the infrared spectra of the complexes with that of the free ligands shows that on complexation two major changes occur. First, the P–aryl grouping frequency observed at ~1085 cm^{-1} in the free ligands shifted to 1100–1110 cm^{-1} on complex formation, which can be taken as an evidence for the coordination of phosphorus to metal [19]. Second, all these ruthenium complexes of ditertiary phosphines depict a sharp band at ~885 cm^{-1} which confirms the chelating behaviour of the ligand [20]. The thiocyanato complexes of ruthenium, [Ru(P–P')$_2$(NCS)$_2$], are of special importance in solving the interesting problem of whether the thiocyanato group is bound to the metal through the nitrogen atom (M–NCS), through the sulphur atom (M–SCN), or through both by means of a bridging structure (M–SCN–M).

It is reported that ν(CN) frequencies are generally lower (below 2100 cm^{-1}) when the coordination is through nitrogen [21]. When the coordination takes place through sulphur ν(CN) are observed above 2100 cm^{-1}. In the complexes [Ru(**1a**)$_2$(NCS)$_2$],

TABLE I. Physical Properties and the Analytical Data Obtained for the Complexes of Ruthenium(II) with Ditertiary Phosphines

Complex[a]	Colour	Decomposition temperature (°C)	Analysis, found (calc.) (%)		
			C	H	Cl
$[Ru(1a)_2Cl_2]$	yellow	274–275	60.2	4.4	6.6
			(60.0)	(4.2)	(6.8)
$[Ru(1a)_2Br_2]$	yellow	250–251	55.1	3.6	
			(55.2)	(3.9)	
$[Ru(1a)_2I_2]$	yellow	285–286	51.2	3.3	
			(51.0)	(3.6)	
$[Ru(1a)_2(NCS)_2]$	cream	260–261	59.5	4.2	10.5
			(59.7)	(4.0)	(10.7)
$[Ru(CO)_2(1a)Cl_2]$	yellow	195–197	50.5	3.0	10.5
			(50.8)	(3.4)	(10.7)
$[Ru(CO)_2(1a)Br_2]$	yellow	215–216	44.4	2.6	
			(44.7)	(2.6)	
$[Ru(CO)_2(1a)I_2]$	yellow	225–226	39.5	2.5	
			(39.8)	(2.6)	
$[Ru(1b)_2Cl_2]$	lemon–yellow	279–280	59.9	4.4	6.7
			(60.0)	(4.6)	(6.8)
$[Ru(1b)_2Br_2]$	yellow	258–259	55.2	3.6	
			(55.3)	(3.9)	
$[Ru(1b)_2I_2]$	dark-yellow	290–291	50.6	3.4	
			(51.0)	(3.6)	
$[Ru(1b)_2(NCS)_2]$	greenish-yellow	266–267	59.5	3.9	
			(59.8)	(4.1)	
$[Ru(CO)_2(1b)Cl_2]$	yellow	201–202	50.5	3.1	10.4
			(50.8)	(3.4)	(10.7)
$[Ru(CO)_2(1b)Br_2]$	yellow	220–221	44.5	2.7	
			(44.8)	(3.0)	
$[Ru(CO)_2(1b)I_2]$	yellow	230–231	39.6	2.4	
			(39.6)	(2.6)	
$[Ru(1c)_2Cl_2]$	lemon–yellow	215–217	54.0	3.3	5.5
			(54.2)	(3.6)	(5.7)
$[Ru(1c)_2Br_2]$	yellow	240–242	54.3	3.1	
			(54.6)	(3.3)	
$[Ru(1c)_2I_2]$	canary-yellow	226–228	47.0	2.9	
			(47.2)	(3.1)	
$[Ru(1c)_2(NCS)_2]$	yellow	220–221	54.0	3.4	
			(54.1)	(3.5)	
$[Ru(CO)_2(1c)(Cl_2)]$	yellow	188–189	47.0	2.7	
			(47.3)	(2.9)	
$[Ru(CO)_2(1c)Br_2]$	yellow	158–159	42.1	2.3	
			(43.2)	(2.6)	
$[Ru(CO)_2(1c)I_2]$	yellow	150–152	37.9	2.1	
			(38.1)	(2.4)	

[a] **1a** = $(m\text{-}FC_6H_4)_2PCH_2CH_2PPh_2$; **1b** = $(p\text{-}FC_6H_4)_2PCH_2CH_2PPh_2$; **1c** = $(m\text{-}CF_3C_6H_4)_2PCH_2CH_2PPh_2$.

$[Ru(\mathbf{1b})_2(NCS)_2]$ and $[Ru(\mathbf{1c})_2(NCS)_2]$ the ν(CN) frequencies were observed at 2080, 2085 and 2040 cm^{-1} respectively, which confirms the N-bonded nature of the thiocyanato group [21]. In addition to that, the vibrations of the isothiocyanato group absorption peaks also appear at ~850 and ~470 cm^{-1} due to ν(C–S) and δ(NCS), respectively.

It has been observed [22] that *cis*-$[M(P{-}P)_2X_2]$ (C_{2v}) octahedral complexes exhibit two infrared active ruthenium–halogen bands in the far-infrared region, whereas *trans*-$[M(P{-}P)_2X_2]$ (D_{4h}) complexes exhibit only one band. The complexes of type $[Ru(P{-}P')_2X_2]$ depict only one band in the far-infrared region (Table II) thereby confirming the *trans* nature of the complexes. These frequencies are consistent with the D_{4h} symmetry of the molecule.

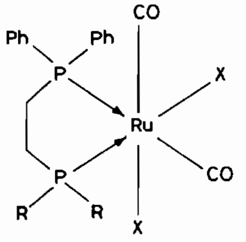
Ruthenium dihalodicarbonyl complexes of the type $[Ru(CO)_2(P{-}P')X_2]$ (X = Cl, Br, I) exhibit two infrared active ν(CO) frequencies in the carbonyl absorption region (Table II). In the far-infrared spectra, these complexes depict two ruthe-

TABLE II. ^{1}H NMR, ν(CO) and ν(Ru–X) Frequencies of Ruthenium(II) Complexes^a

Compound	^{1}H NMR (δ ppm)		ν(CO) (cm^{-1})	ν(Ru–X) (cm^{-1})
	Aromatic phenyl protons	Methylene protons		
$[Ru(\mathbf{1a})_2Cl_2]$	7.60–6.75(m)	2.80–2.40(b)		335
$[Ru(\mathbf{1a})_2Br_2]$	7.65–7.70(m)	2.60–2.35(b)		295
$[Ru(\mathbf{1a})_2I_2]$	7.60–7.80(m)	2.60–2.30(b)		–
$[Ru(\mathbf{1a})_2(NCS)_2]$				
$[Ru(CO)_2(\mathbf{1a})Cl_2]$	7.70–6.80(m)	2.30–2.10(b)	2030(s), 1975(s)	335, 295
$[Ru(CO)_2(\mathbf{1a})Br_2]$	7.60–6.75(m)	2.25–1.95(b)	2060(s) 1990(s)	290, 260
$[Ru(CO)_2(\mathbf{1a})I_2]$	7.65–6.60(m)	2.30–2.00(b)	2045(s), 1955(s)	
$[Ru(\mathbf{1b})_2Cl_2]$	7.70–7.90(m)	2.90–2.45(b)		330
$[Ru(\mathbf{1b})_2Br_2]$	7.75–7.85(m)	2.60–2.35(b)		300
$[Ru(\mathbf{1b})_2I_2]$	7.80–7.95(m)	2.70–2.30(b)		
$[Ru(\mathbf{1b})_2(NCS)_2]$				
$[Ru(CO)_2(\mathbf{1b})Cl_2]$	7.70–6.90(m)	2.35–2.20(b)	2060(s), 1990(s)	335, 290
$[Ru(CO)_2(\mathbf{1b})Br_2]$	7.75–6.85(m)	2.40–2.00(b)	2050(s), 1975(s)	310, 285
$[Ru(CO)_2(\mathbf{1b})I_2]$	7.70–6.70(m)	2.35–2.10(b)	2040(s), 1960(s)	
$[Ru(\mathbf{1c})_2Cl_2]$	7.70–6.95(m)	2.95–2.55(b)		320
$[Ru(\mathbf{1c})_2Br_2]$	7.75–7.00(m)	2.90–2.50(b)		
$[Ru(\mathbf{1c})_2I_2]$	7.70–7.05(m)	2.85–2.45(b)		
$[Ru(\mathbf{1c})_2(NCS)_2]$	7.80–7.15(m)	2.90–2.35(b)		
$[Ru(CO)_2(\mathbf{1c})(Cl_2)]$	7.75–6.95(m)	2.50–2.25(b)	2050(s), 1970(s)	340, 290
$[Ru(CO)_2(\mathbf{1c})Br_2]$	7.70–6.90(m)	2.40–2.05(b)	2060(s), 1975(s)	305, 290
$[Ru(CO)_2(\mathbf{1c})I_2]$	7.80–6.95(m)	2.45–2.15(b)	2045(s), 1960(s)	

^{a}m = multiplet, b = broad, s = sharp.

nium–halide bands. Ditertiary phosphines can form both *cis* and *trans* octahedral $[Ru(CO)_2(P–P'X)_2$ complexes with ruthenium dihalodicarbonyls. It is known that *cis*-octahedral complexes exhibit two infrared active ν(CO) frequencies, whereas *trans* complexes show only one infrared active ν(CO) frequency [23]. Since two ν(CO) were observed, these complexes have presumably *cis*-octahedral structures:



(R = m-FC_6H_4, p-FC_6H_4, m-$CF_3C_6H_4$)

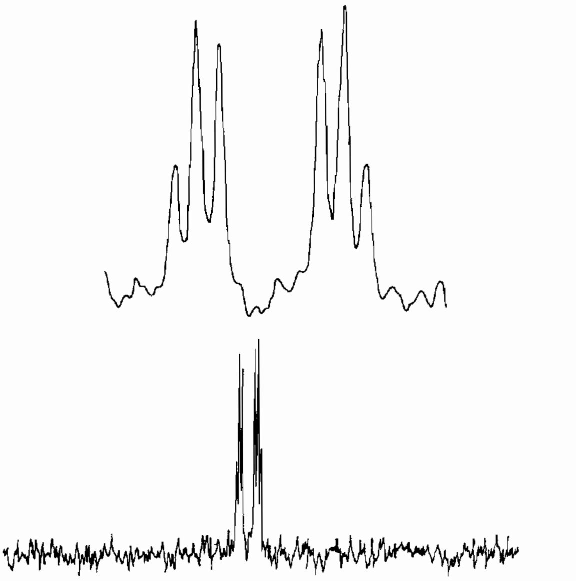
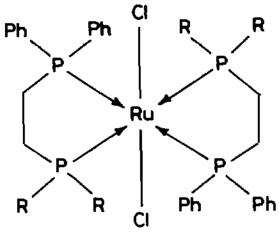


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Ru(\mathbf{1c})_2Cl_2]$ obtained at 40.32 MHz.

All these complexes of ruthenium halides and dihalodicarbonyls were found to be non-electrolytes in nitromethane solution.

^{1}H NMR spectra of all these complexes show a downfield shift of aromatic as well as aliphatic protons as compared to free ligand spectra. In the free ligand spectra the methylene protons are observed as a triplet due to the nuclear splitting of protons by phosphorus. But on complexation these methylene protons are observed as a broad peak.

$^{31}P\{^1H\}$ NMR spectra of the complexes $[Ru(\mathbf{1a})_2Cl_2]$ and $[Ru(\mathbf{1b})_2Cl_2]$ are complicated and mainly consist of three triplets in the ratio 1:2:1. Some additional peaks were also observed indicating the presence of more than one species. But in the case of the complex $[Ru(1c)_2X_2]$ (X = Cl or Br), two triplets (Fig. 1) were observed at $\delta(PPh_2) = +45.66$ ppm and $\delta P(C_6H_4F_3C\text{-}m)_2 = +49.17$ ppm with $^2J(P\text{–}P') = 21.98$ Hz for the chloride complex and $\delta(PPh_2) = +50.4$ ppm and $\delta P(C_6H_4F_3C\text{-}m)_2 = +49.88$ ppm, $^2J(P\text{–}P') = 21.13$ Hz for the bromide complex. The $^2J(P\text{–}P')$value is in accordance with the typical $^2J(P\text{–}P')$ value for the coupling constant of non-equivalent phosphorus nuclei *cis* to one another in ruthenium(II)–tertiary phosphine complexes. (A value about ten times larger is expected for *trans* P–P′ coupling [5]). Thus the $^{31}P\{^1H\}$ NMR spectra clearly suggest the presence of only one isomer, *i.e.* the all *trans* arrangement:



in which $(m\text{-}CF_3C_6H_4)_2P$ is *trans* to $(m\text{-}CF_3C_6H_4)_2P$ and Ph_2P *trans* to Ph_2P

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