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[2-{Di(p-tolyl)phosphino}ethyl] Diphenylphosphine and [2-{Di(m-tolyl)phosphino}ethyl] Diphenylphosphine Complexes of Ruthenium(II) Halides and Dihalodicarbonyls

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Abstract

The ditertiary phosphines; [2-{di(p-tolyl)phosphino}ethyl] diphenylphosphine (pptpf) and [2-{di(m-tolyl)phosphino}ethyl] diphenylphosphine (pmtpf) complexes of ruthenium of the type: [Ru(pptpf)$_2$X$_2$], [Ru(pmtpf)$_2$X$_2$] (where X = Cl, *Br*, I or NCS), [Ru(CO)$_2$X$_2$(pptpf)] and [Ru(CO)$_2$X$_2$(pmtpf)] (where X = Cl, Br or I) were prepared. *trans*-octahedral structure for [Ru(pptpf)$_2$X$_2$] and [Ru(pmtpf)$_2$X$_2$] complexes and *cis*-octahedral structure for [Ru(CO)$_2$X$_2$(pptpf)] and [Ru(CO)$_2$X$_2$(pmtpf)] complexes on the basis of IR and proton NMR data have been suggested. In all these complexes ligands (pptpf) and (pmtpf) act as chelating ditertiary phosphines.

Introduction

During the last few years we have been interested in the synthesis of new ditertiary phosphine ligands with different organic substituents on the donor phosphorous atoms, which will impart either different solubilities or different electronic and steric properties of their complexes. We have synthesized a series of new ligands of the type $R_2P\text{-}CH_2\text{-}CH_2PPh_2$ (R = m- or p-$CH_3C_6H_4$ [1, 2] m-$CF_3C_6H_4$ [3] or p-F C_6H_4 [3] groups) and discussed their coordination chemistry with nickel, palladium and platinum halides [1–3]. This paper presents a comparative study of the reactions of two ditertiary phosphines: (p- or m-$CH_3C_6H_4)_2P{-}CH_2{-}CH_2{-}PPh_2$ with ruthenium halides and ruthenium carbonyl halides with the objective of observing the effect of different organic groups on donor phosphorus atoms in the solubilities of the complexes. Ditertiary phosphine complexes ($Ph_2P{-}CH_2{-}CH_2PPh_2$) of the ruthenium have been extensively studied [4–10].

Experimental

Materials

All the chemicals used were of analytical grade. Nitromethane was washed with 5% aqueous sulphuric acid and 5% aqueous sodium bicarbonate solution, the fraction boiling at 101 °C being collected. All the solvents were dried and purified by standard methods [11]. All the reactions and subsequent handling were carried out in nitrogen.

The ligands [2-{di(p-tolyl)phosphino}ethyl] diphenylphosphine (pptpf) and [2-{di(m-totyl)phosphono}ethyl] diphenylphosphine were prepared by the methods reported earlier [2, 12]; dichlorodicarbonylruthenium (II) [Ru(CO)$_2$Cl$_2$] was prepared by a literature method [13].

Elemental Analysis and Physical Measurements

Carbon and hydrogen were estimated by a combustion method, phosphorus was estimated by ammonium phosphomolybdate. IR spectra were recorded on a Perkin–Elmer 621 Spectrophotometer. The ^{1}H NMR were recorded in CDCl$_3$ solution on Perkin–Elmer R-32 instrument. The molecular conductance was measured on an Elico-conductivity bridge type CM 82 T.

Preparation of Complexes

Ruthenium(II) halide complexes

[Ru(pptpf)$_2$Cl$_2$]. RuCl$_3$·3H$_2$O (0.261 g, 1.0 mmol) in water (10 ml) was added to [2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine (pptpf) (0.853 g, 2.0 mmol) in ethanol (100 ml) and the solution was refluxed for 3 h. The black solution gradually becomes green and finally cleared to light yellow. Dilution with water gave a precipitate, which after crystallization from chloroform gave a light-yellow crystalline compound.

[Ru(pptpf)$_2$Br$_2$]. [Ru(pptpf)$_2$Cl$_2$] (0.341 g, 0.33 mmol) was refluxed in ethanol (50 ml) with potassium bromide (20 fold excess) for 36 h. The solution slowly changed colour from light to dark yellow.

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After cooling to room temperature, solvent was removed from the reaction mixture under reduced pressure. The residue so obtained was washed with water and the complex was extracted with benzene to give a light-yellow complex.

[Ru(pptpf)$_2$I$_2$]. [Ru(pptpf)$_2$Cl$_2$] (0.341 g, 0.33 mmol) was refluxed in ethanol (50 ml) with potassium iodide (20 fold excess) for 50 h. After cooling to room temperature, solvent was removed from the reaction mixture under reduced pressure. The complex was again extracted with benzene to give a yellow complex.

[Ru(pptpf)$_2$(NCS)$_2$]. This compound was prepared as above, potassium thiocyanate (20 fold excess) being used and a cream complex was isolated.

The complexes of [2-{di(*m*-tolyl)phosphino}ethyl]diphenylphosphine (pmtpf) with ruthenium(II) halides of type [Ru(pmtpf)$_2$X$_2$] (X = Cl, Br, I or NCS) were synthesized similar to the procedure adopted for the corresponding [2-{di(*p*-tolyl)phosphino}ethyl]diphenylphosphine complexes.

Dihalodicarbonyl ruthenium(II) complexes

[Ru(CO)$_2$Cl$_2$(pptpf)]. Dichlorodicarbonyl ruthenium(II) (0.455 g, 2.0 mmol) was dissolved in 30 ml of methanol and the solution was refluxed for 2 h. To this solution [2-{di(*p*-tolyl)phosphino}ethyl]-diphenylphosphine (pptpf) (0.853 g, 2.0 mmol) was added and refluxed for 1 h. A light yellow precipitate was formed, which was separated, washed with petroleum ether (60–80 °C) and dried under vacuo to give light yellow complexes.

[Ru(CO)$_2$Br$_2$(pptpf)]. [Ru(CO)$_2$Cl$_2$(pptpf)] (0.327 g, 0.5 mmol) was heated under reflux in 2-methoxyethanol (40 ml) with potassium bromide (20 fold excess) for 9–10 h. The reaction mixture was then cooled to room temperature and solvent was removed from the reaction mixture. The solid so obtained was washed with water and n-hexane and dried *in vacuo* to give a yellow complex.

[Ru(CO)$_2$I$_2$(pptpf)]. This compound was prepared as above, potassium iodide (20 fold excess) being used, and a yellow complex was isolated.

TABLE I. Properties of Ruthenium(II) Complexes of [2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine (pptpf) and [2-{di-(m-tolyl)phosphine}ethyl]diphenyl Phosphine (pmtpf).

Complex	Colour	Dec. Temp. °C	Yield %	Analysis % Found (Calcd.)		
				C	H	P
[Ru(pptpf)$_2$Cl$_2$]	light yellow	290	75	65.45	5.3	11.8
				(65.6)	(5.5)	(12.1)
[Ru(pptpf)$_2$Br$_2$]	light yellow	269–270	65	60.1	4.95	10.9
				(60.4)	(5.1)	(11.1)
[Ru(pptpf)$_2$I$_2$]	yellow	310–312	60	55.6	4.6	10.1
				(55.7)	(4.7)	(10.25)
[Ru(pptpf)$_2$(NCS)$_2$]	cream	280	65	(67.4)	5.3	11.9
				(67.6)	(5.6)	(12.2)
[Ru(pmtpf)$_2$Cl$_2$]	light yellow	261	60	65.5	5.6	11.95
				(65.6)	(5.5)	(12.1)
[Ru(pmtpf)$_2$Br]	yellow	241	70	60.25	4.9	10.8
				(60.4)	(5.1)	(11.1)
[Ru(pmtpf)$_2$I$_2$]	yellow	305–306	62	55.55	4.6	10.0
				(55.7)	(4.7)	(10.25)
[Ru(pmtpf)$_2$(NCS)$_2$]	cream	257–258	67	67.4	5.45	12.0
				(67.6)	(5.6)	(12.2)
[Ru(CO)$_2$Cl$_2$(pptpf)]	yellow	212	70	54.9	4.2	9.3
				(55.05)	(4.3)	(9.5)
[Ru(CO)$_2$Br$_2$(pptpf)]	yellow	224	63	48.35	3.6	8.15
				(48.5)	(3.8)	(8.3)
[Ru(CO)$_2$I$_2$(pptpf)]	yellow	232	55	42.7	3.2	7.1
				(43.0)	(3.4)	(7.4)
[Ru(CO)$_2$Cl$_2$(pmtpf)]	yellow	185	65	54.75	4.1	9.4
				(55.05)	(4.3)	(9.5)
[Ru(CO)$_2$Br$_2$(pmtpf)]	yellow	193	58	48.4	3.6	8.1
				(48.5)	(3.8)	(8.3)
[Ru(CO)$_2$I$_2$(pmtpf)]	yellow	208	60	42.8	3.2	9.2
				(43.0)	(3.4)	(9.5)

The complexes of [2-{di(*m*-tolyl)phosphino}-ethyl]diphenylphosphine (pmtpf) with dihalodicarbonyl ruthenium(II) of the type [Ru(CO)$_2$X$_2$-(pmtpf)] (where X = Cl, Br or I) were synthesized by a method similar to that adopted for the corresponding (pptpf) complexes.

The analytical data of all these complexes are given in Table I.

Results and Discussion

The reaction of [2-{di(*p*-tolyl)phosphino}ethyl]-diphenylphosphine (pptpf) and [2-{di(*m*-tolylphosphino}ethyl]diphenylphosphine (pmtpf) with RuCl$_3$·3H$_2$O and Ru(CO)$_2$Cl$_2$ in ethanol solutions yielded the complexes of type [Ru(pptpf)$_2$Cl$_2$], [Ru-(pmtpf)$_2$Cl$_2$], [Ru(CO)$_2$Cl$_2$(pptpf)] and [Ru(CO)$_2$Cl$_2$-(pmtpf)]. The corresponding bromo, iodo and thiocyanate complexes were easily obtained by metathetical exchange reactions, as described above.

The IR spectra of these complexes were very similar to the free ligand spectra. The band due to P–aryl grouping at ~ 1090 cm^{-1} in the free ligand has shifted to 1100 cm^{-1} on complex formation, indicating the coordination through phosphorus atoms [14]. Similarly, a band at ~ 880 cm^{-1} appeared which shows chelating bidentate behaviour of the ligands (pptpf) and (pmtpf) in all these complexes [15].

In the case of thiocyanato complexes, the SCN group may coordinate to metal through the nitrogen or sulphur atom, or both. It is well known [16] that the CN stretching frequencies are generally lower in N–bonded complexes (below 2100 cm^{-1}) than in S-bonded complexes (above 2100 cm^{-1}). In [Ru-(pptpf)$_2$(NCS)$_2$] and [Ru(pmtpf)$_2$(NCS)$_2$] complexes, sharp bands at 2050 cm^{-1} and at 2070 cm^{-1} respectively were observed and assigned to the N-bonded thiocyanato groups in these complexes. Two additional vibrations of the isothiocyanato groups also appear due to ν(C–S) at 845 cm^{-1} and at 840 cm^{-1} and δ(NCS) at 470 cm^{-1} and at 475 cm^{-1} in [Ru-(pptpf)$_2$(NCS)$_2$] and [Ru(pmtpf)$_2$(NCS)$_2$] complexes, respectively.

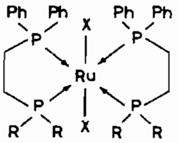
In general ditertiaryphosphines (P–P) forms both *cis*- and *trans*-octahedral [(Ru(CO)$_2$X$_2$(P–P)] complexes with ruthenium(II) dihalodicarbonyls. It is known [16, 17] that *cis*-octahedral complexes exhibits two infrared active ν(CO) frequencies, whereas *trans*-complexes show only one IR active ν(CO) frequency. In the complexes [Ru(CO)$_2$X$_2$(pptpf)] and [Ru(CO)$_2$X$_2$(pmtpf), (where X = Cl, Br or I) we observed two bands in the 2200–1900 cm^{-1} region (Table II) due to carbonyl group absorptions, and so they presumably have the *cis*-octahedral structure.

As predicted from group theory [16] *cis*-[MX$_2$L$_4$]-(C$_{2v}$) octahedral complexes should exhibit two IR active ruthenium–halogen bands, whereas *trans*-[MX$_2$L$_4$](D$_{4h}$) should give only one band in far–IR spectra. Only one band has been observed in the far–IR spectra of [Ru(pptpf)$_2$X$_2$] and [Ru-(pmtpf)$_2$X$_2$] (where X = Cl, Br, I or (NCS)) complexes (Table II) indicating *trans*-configuration of these complexes (Scheme 1), whilst two ν(Ru–X)

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

Compound	^{1}H NMR (δ ppm)		ν(CO) cm^{-1}	ν(Ru–X) cm^{-1}
	Aromatic protons	methyl protons		
[Ru(pptpf)$_2$Cl$_2$]	7.35(m)	2.3(s)	–	330(s^1)
[Ru(pptpf)$_2$Br$_2$]	7.4(m)	2.35(s)	–	290(s^1)
[Ru(pptpf)I$_2$]	7.35(m)	2.3(s)	–	–
[Ru(pptpf)$_2$(NCS)$_2$]	7.3(m)	2.4(s)	–	320(s^1)
[Ru(pmtpf)$_2$Cl$_2$]	7.3(m)	2.35(s)	–	335(s^1)
[Ru(pmtpf)$_2$Br$_2$]	7.4(m)	2.35(s)	–	295(s^1)
[Ru(pmtpf)$_2$I$_2$]	7.35(m)	2.3(s)	–	–
[Ru(pmtpf)$_2$(NCS)$_2$]	7.35(m)	2.4(s)	–	325(s^1)
[Ru(CO)$_2$Cl$_2$(pptpf)]	7.3(m)	2.3(s)	2040(s^1), 1980(s^1)	330(s), 295(s^1)
[Ru(CO)$_2$Br$_2$(pptpf)]	7.25(m)	2.35(s)	2100(s^1), 1985(s^1)	265(s^1)
[Ru(CO)$_2$I$_2$(pptpf)]	7.3(m)	2.35(s)	2050(s^1), 1965(s^1)	–
[Ru(CO)$_2$Cl$_2$(pmtpf)]	7.25(m)	2.2(s)	2075(s^1), 1990(s^1)	335(s), 290(s^1)
[Ru(CO)$_2$Br$_2$)pmtpf)]	7.3(m)	2.35(s)	2100(s^1), 2010(s^1)	260(s^1)
[Ru(CO)$_2$I$_2$(pmtpf)]	7.35(m)	2.35(s)	2060(s^1), 1970(s^1)	–

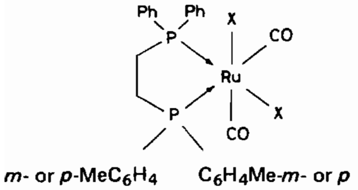
^{a}(m) = multiplet, (s) = singlet, (s^1) = strong, (pptpf) = [2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine, (pmtpf) = [2-{di-(m-tolyl)phosphino}ethyl]diphenylphosphine.



where X = Cl, Br, I or NCS
R = *m*- or *p*-MeC_6H_4

Scheme 1.

bands in $[Ru(CO)_2X_2(pptpf)]$ and $[Ru(CO)_2X_2(pmtpf)]$ (where X = Cl or Br) complexes show their *cis*-configuration (scheme 2). In addition the $[Ru(pptpf)_2X_2]$ and $[Ru(pmtpf)_2X_2]$ (where X = Cl or Br) complexes were found unreactive towards $LiAlH_4$, confirming the *trans*-nature of these complexes [5].



where X = Cl, Br or I

Scheme 2.

All these complexes of Ru(II) halides and dihalodicarbonyls of (pptpf) and (pmtpf) were found to be non-electrolyte in nitromethane solution.

In ^1H NMR spectra of free ligands (pptpf) and (pmtpf)) aromatic protons give a complex multiplet at $\delta7.3$ and $\delta7.25$, the methylene protons give a broad spectrum at about $\delta2.0$ and $\delta2.05$ and methyl resonance occurs at $\delta2.23$ and $\delta2.4$, respectively. All the complexes reported in this paper showed downfield shift of aromatic protons (at $\delta7.4$–7.25) and methyl resonances (at $\delta2.4$–2.2), compared to those of free ligand (Table II).

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