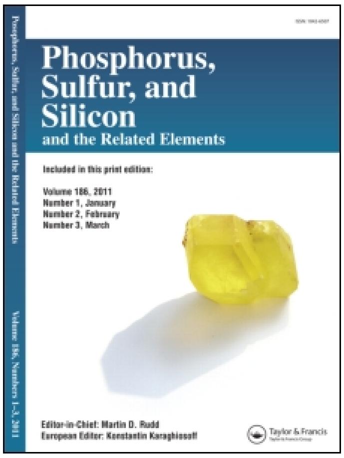

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Synthesis and Characterization of Tris(Triphenylphosphine) Ruthenium (II) Alkylene Dithiophosphate and Their Halide Derivatives

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SYNTHESIS AND CHARACTERIZATION OF TRIS(TRIPHENYLPHOSPHINE) RUTHENIUM (II) ALKYLENE DITHIOPHOSPHATE AND THEIR HALIDE DERIVATIVES

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Reactions of $(Ph_3P)_3RuCl_2$ with the ammonium salt of alkylene dithiophosphoric acids in 1:1 and 1:2 stoichiometry gave complexes of the type $(Ph_3P)_3Ru(Cl)[S_2POGO]$(A) and $(Ph_3P)_3Ru[S_2\overline{POGO}]_2$(B), G= $-CMe_2CMe_2-$,$-CH_2CMe_2CH_2-$, $-CH_2CEt_2CH_2-$ and $-CMe_2CH_2CHMe-$. Molecular weight determinations and IR and NMR (^1H and ^{31}P) spectral data indicate a hexacoordinated octahedral structure. The dithioligand in (B) complexes show monodentate and bidentate chelating.

Keywords: Dithiophosphate; Ruthenium; homogenous catalysts

INTRODUCTION

Compared to the few literature references on ruthenium complexes of dialkyl dithiophosphoric acids[1,2], no work has been done on the cyclic derivatives of alkylene dithiophosphoric acids $\overline{OGOP}(S)SH$, which show diverse bonding possibilities as monodentate[3] and bidentate[4–6] chelating. So, in view of the exciting chemistry and various applications of the arene-ruthenium complexes such as $[RuCl_2(PR_3)(arene)]$ and $Cl_2Ru(arene)$[7,8] which are used as homogenous catalysts. It was thought worthwhile to synthesis bis as well as mixed chloro alkylene dithiophos-

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phate derivatives of ruthenium and to investigate their various physico chemical properties.

RESULTS AND DISCUSSION

Reactions of $(Ph_3P)_3RuCl_2$ with ammonium salt of alkylene dithiophosphoric acid in 1:1 and 1:2 stoichiometry gave triphenylphosphine ruthenium (II) alkylene dithiophosphate complexes of the type $(Ph_3P)_3Ru[S_2\overline{POGO}]_2$ and $(Ph_3P)_3Ru(Cl)[S_2\overline{POGO}]$ G= $-CMe_2CMe_2$ -,$-CH_2CMe_2CH_2$-, $-CH_2CEt_2CH_2$- and $-CMe_2CH_2CHMe$-. The above complexes are dark greenn or brown colored powdery solids, except $(Ph_3P)_3Ru(Cl)[S_2\overline{POCMe_2CMe_2O}]$ which is a sticky solid, soluble in organic solvents like benzene, chloroform and dichloromethane but insoluble in n-hexane However, attempts to crystallize the solid compounds from benzene/n-hexane mixture were unsuccessful.

Molecular weights (Table I), determined cryoscopically in benzene, indicated the monomeric nature of these products.

IR SPECTRA

IR spectra of these derivatives (Table II) exhibit bands in the region 1115-1168 and 802–880 cm^{-1} which may be assigned to v(P)-O-C and vP-O-(C) streching mode respectively[9,10]. The bands present in the region 945–992 cm^{-1} may be ascribed to dioxaphospholane and dioxaphosphorinane ring vibrations[11,12]. The bands due to vP=S are observed in the region 662–694 cm^{-1}. The bands attributable to v P-S vibrations[13] are present in the region 511–571 cm^{-1}. Interestingly, the IR spectra of (B) complexes in the area 500–700 cm^{-1} show additional bands than those of (A) complexes. This appears to be diagnostic of unidentate and bidentate to these metals as reported before[14,15]. The bands of weak to medium intensity in the regions 371–373 and 419–458 cm^{-1} may be assigned to Ru-Cl and Ru-S, respectively [16,17].

TABLE I Synthetic and analytical data of tris (triphenylphosphine) ruthenium (II) alkylene dithiophosphates and their chloro derivatives

Compound No.	*Reactants (g)*		*Molar Ratio*	*Products/ physical state*	*Yield %*	*M.P. °C*	*Analysis (%) Found/ (Calc)*			*Mol. wt. Found (Calc.)*
	$(Ph_3P)_3RuCl_2$	$NH_4S_2\overline{POGO}$ G =					*P*	*S*	*Cl*	
1		$-CMe_2CMe_2-$	1:1	$(Ph_3P)_3Ru(Cl)[S_2\overline{POCMe_2CMe_2O}]$	87.7	---	2.54	5.53	2.89	1125.2
	2.68	0.64		brown sticky solid			(2.73)	(5.64)	(3.13)	(1133.9)
2		$-CMe_2CMe_2-$	1:2	$(Ph_3P)_3Ru[S_2\overline{POCMe_2CMe_2O}]_2$	88.5	98	4.62	9.63	---	1298.37
	0.89	0.42		green powdery solid			(4.71)	(9.77)		(1309.65)
3		$-CH_2CMe_2CH_2-$	1:1	$(Ph_3P)_3Ru(Cl)[S_2\overline{POCH_2CMe_2CH_2O}]$	96.5	82	2.58	5.66	2.86	1102.6
	1.17	0.26		brown powdery solid			(2.75)	(5.71)	(3.16)	(1120.05)
4		$-CH_2CMe_2CH_2-$	1:2	$(Ph_3P)_3Ru[S_2\overline{POCH_2CMe_2CH_2O}]_2$	94.8	120	4.53	9.76	---	1263.6
	1.18	0.52		green powdery solid			(4.82)	(9.98)		(1281.95)
5		$-CH_2CEt_2CH_2-$	1:1	$(Ph_3P)_3Ru(Cl)[S_2\overline{POCH_2CEt_2CH_2O}]$	95	103	2.62	5.41	2.74	1153.45
	1.21	0.30		green powdery solid			(2.69)	(5.57)	(3 09)	(1147.9)

Compound No.	Reactants (g)		Molar Ratio	Products/ physical state	Yield %	M.P. °C	Analysis (%) Found/ (Calc)			Mol. wt. Found (Calc.)
	$(Ph_3P)_3RuCl_2$	$NH_4S_2\overline{POGO}$ G =					P	S	Cl	
6		$-CH_2CEt_2CH_2-$	1:2	$(Ph_3P)_3Ru[S_2\overline{POCH_2CEt_2CH_2O}]_2$	93.6	160	4.46	9.30	---	1311.25
	0.79	0.40		brown powdery solid			(4.62)	(9.57)		(1337.3)
7		$-CMe_2CH_2CHMe-$	1:1	$(Ph_3P)_3Ru(Cl)[S_2\overline{POCMe_2CH_2CHMeO}]$	91.4	105	2.54	5.39	2.88	1119.72
	0.40	0.095		green powdery solid			(2.72)	(5.64)	(3.13)	(1134.08)
8		$-CMe_2CH_2CHMe-$	1:2	$(Ph_3P)_3Ru[S_2\overline{POCMe_2CH_2CHMeO}]_2$	90.6	115	4.58	9.68	---	1289.6
	0.94	0.45		brown powdery solid			(4.71)	(9.77)		(1309.66)

TABLE II IR Spectral data of tris(triphenylphosphine)ruthenium (II) of alkylene dithiophosphates and their chloro derivatives

Compound No.	*Compound*	*(P)-O-C*	*P-O-(C)*	*Ring Vibration*	ν *P =S*	ν *P-S*	*Ru-S*	*Ru-Cl*
1	$(Ph_3P)_3Ru(Cl)[S_2\overline{POCMe_2CMe_2O}]$	1163 m	848 m	959 m	691s	544 s	417 m	371s
2	$(Ph_3P)_3Ru[S_2\overline{POCMe_2CMe_2O}]_2$	1168 s	844 m	953 m	674 s	531 s	429 s	---
					635 s	575 s		
3	$(Ph_3P)_3Ru(Cl)[S_2\overline{POCH_2Me_2CH_2O}]$	1166 m	850 m	972 m	688 s	540 m	418 m	370 w
4	$(Ph_3P)_3Ru[S_2\overline{PO\ CH_2Me_2CH_2O}]_2$	1160 m	840 m	969 s	600 m	511 m	458 m	---
					693 m	532 m		
5	$(Ph_3P)_3Ru(Cl)[S_2\overline{POCH_2CEt_2CH_2O}]$	1155 m	803 w	967 m	694 m	542 m	450 m	---
6	$(Ph_3P)_3Ru[S_2\overline{POCH_2CEt_2CH_2O}]_2$	1156 s	802 s	994 s	694 s	520 s	459 m	---
					606 m	533 s		
7	$(Ph_3P)_3Ru(Cl)[S_2\overline{POCMe_2CH_2CHMeO}]$	1117 m	815 m	953 m	667 m	539 m	419 w	373 m
8	$(Ph_3P)_3Ru[S_2\overline{PO\ CMe_2CH_2CHMeO}]_2$	1115 m	880 m	945 s	688 m	540 m	420 m	---
					723 s	579 m		

s = strong, m = medium, w = weak

^{1}H NMR SPECTRA

The ^{1}H NMR spectra (Table III) of [A] complexes exhibited the expected integrations and peak multiplicities. Only one set of resonances for equivalent protons was observed. The spectra of [B] complexes show two sets of resonances for the glycoxy group because they are in non-equivalent environments due to the monodentate and bidentate behavior of these ligands as it will be shown in ^{31}P spectra.

The complex multiplet due to the protons of triphenylphosphine/ – ruthenium mioties appear in the region 7.02–7.76 ppm.

^{31}P NMR SPECTRA

The ^{31}P NMR spectra (Table III) give an interesting result in [A] and [B] complexes.

In [A] derivatives, it shows two peaks one for triphenylphosphine at −111 and the other peaks are down field (~ 49.11–29.0 ppm) from the position in the corresponding parent dithiophosphoric acids. These values, are consistent with a general bidentate behavior of dithiophosphate moieties[18].

In [B] complexes, it shows three peaks:

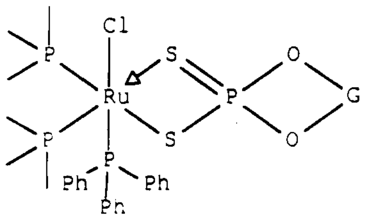
i) The peak of triphenylphosphine at – 111

ii) The second peak in the range of 47.36–15.73 ppm with respect to parent dithiophosphoric acids, suggesting bidentate nature of ligand moiety

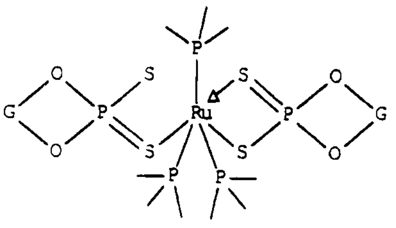
iii) The third peak in the range of 20–24 ppm with respect to the free acids.

These indicate the unidentate behavior of the ligands, since the resonance for the complexes and the ligands are approximately at a similar position [1,3,20,21].

Thus, the above IR and NMR spectral studies show that the dithioligand in [A] complexes are only bidentate but in [B] derivatives it behaves in a chelating bidentate and monodentae fashion with hexacoordinated metal atom in both [A] and [B] complexes.



Complex[A].



Complex [B].

EXPERIMENTAL

Owing to the hydrolyzable nature of starting materials, stringent precautions were taken to exclude the moisture. Solvents (benzene, chloroform, dichloromethane and n-hexane) were dried by standard methods. Glycols were purified by distillation. Tris(triphenylphosphine)ruthenium (II) dichloride (Strem) was used as such. Ammonium salts of alkylene dithiophosphoric acids were prepared by the methods reported in the literature[9]. Sulfur was estimated gravimetrically as barium sulphate. Chlorine was estimated by Volhard's method, phosphorus estimated as ammonium magnesium phosphate hexahydrate.

IR spectra were recorded as Nujol mulls using Perkin-Elmer 2000 FT IR in the range 4000–200 cm^{-1}, using CsI cells. ^1H NMR and ^{31}P spectra were recorded in $CDCl_3$ using Brucker AC 250 FT NMR spectrometer using TMS and trimethylphosphite as external standards respectively.

Synthetic Methods

Reaction of tris(triphenylphosphine) ruthenium (II) dichloride with O, O' tetramethylene dithiophosphate in a 1:1 molar ratio

Tris(triphenylphosphin) ruthenium (II) dichloride (2.68 g) dissolved in dichloromethane (~20 cm^3) was added to a suspension of ammonium O, O' tetramethylene dithiophosphate (0.64 g) in benzene (~30 cm^3). The reaction mixture was stirred for 4 hours and boiled for half an hour. The mixture color turned to brown. The product was separated by filtration, washed several times with n-hexane and dried under reduced pressure to yield a brown sticky solid compound (2.93g, 93%).

Analytical and other relevant data are given in Table I.

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