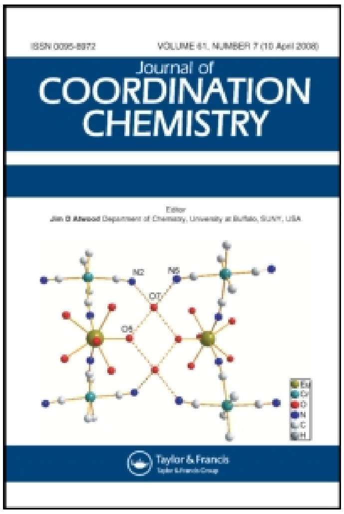

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SOME COMPLEXES OF RUTHENIUM(II) AND (III) WITH MONOTERTIARY PHOSPHINES AND ARSINES

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The complexes $RuCl_2(PPh_3)_3$ and $RuCl_3(AsPh_3)_2(MeOH)$ were employed as convenient starting materials. Methods were developed to prepare *cis-* or *trans-*isomers of the type $RuCl_2L_4$ (L = $AsMePh_2$, $AsMe_2Ph$) starting from $RuCl_2(PPh_3)_3$. Meridonial complexes of the type $RuCl_3L_3$ (L = PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$) were obtained by the reaction of Wilkinson's green complex, $RuCl_3(AsPh_3)_2(MeOH)$ with an excess of L in benzene. In the presence of a large excess of methyldiphenylphosphine in benzene, a five coordinate complex $RuCl_2(PMePh_2)_3$ was obtained. The temperature of the reaction and solvent decide the nature of the reaction product. Thus a polymeric complex of the composition $[RuCl_2(AsPh_3)_2]_n$ was obtained from $RuCl_3(AsPh_3)_2(MeOH)$ with triphenylarsine in boiling propanol. The reaction of $RuCl_3.3H_2O$ with PPh_3 and then $AsPh_3$ in propanol gave mixed ligand polymers of the type $[RuCl_2(PPh_3)(AsPh_3)]_n$.

INTRODUCTION

A large number of ruthenium(II) and ruthenium(III) compounds with tertiary phosphines and arsines were reported in the last two decades. The reaction of ruthenium trichloride with tertiary phosphines and arsines is very much governed by reaction conditions such as the nature of the solvent, stoichiometry of the reaction, and the time of reaction. The reaction of ruthenium trichloride trihydrate with triphenylphosphine in methanol,[1] ethanol[2] or isopropanol[2] for several hours at reflux temperatures gave $RuCl_2(PPh_3)_3$, whereas shaking the reaction mixture at room temperature resulted in the formation of $RuCl_2(PPh_3)_4$.[1] The polymeric species $[RuCl_2(PPh_3)_2]_n$[2] was obtained when the same reaction was carried out in isobutanol or cyclohexanol at reflux.

Very few tertiary arsine complexes of ruthenium(II) were reported. The interaction of ruthenium trichloride trihydrate with dimethylphenylarisine[3] in methanol for several hours at reflux yielded *cis-* and *trans-*$RuCl_2(AsMe_2Ph)_4$. The complex $RuCl_2(AsMePh_2)_4$ was obtained by the interaction of $AsMePh_2$[4] with $RuCl_3$ in alcohol at reflux. Refluxing triphenylarsine in isobutanol with $RuCl_3.3H_2O$ yielded a chlorobridged dimer$[RuCl_2(AsPh_3)_2]_2$.[5] Under acid conditions the reaction of $RuCl_3.3H_2O$ with $AsEtPh_2$ yielded a triple chlorobridged cationic dimer $[Ru_2Cl_3(AsEtPh_2)_6]Cl$.[6]

The synthesis of a wide range of ruthenium(II) complexes containing tertiary phosphines or arisines was achieved[1,7] by the displacement of the phosphine ligand in the complex $RuCl_2(PPh_3)_3$ by nitriles, aromatic amines, ketones, β-diketones, carboxylic acids and cyclopentadiene.

In contrast to ruthenium(II), relatively few ruthenium(III) complexes containing monotertiary phosphines or arsines were reported. The complexes include the series *mer*-RuX_3L_3 (L = PMe_2Ph, PEt_2Ph, PBu^n_2Ph, PPh_3,[8]) $RuX_3(EPh_3)_2S$ (E = P or As; S = MeOH[1,9] $MeNO_2$,[10] Me_2CO,[1] $AsPh_3$),[11] the anions *trans*-$[RuX_4L_2]^-$ (L = PPh_3, PMe_2Ph, PEt_3, $AsPh_3$), and the binuclear complexes $[RuCl_3(PR_3)_2]_2$ and $Ru_2Cl_5(PR_3)_4$ (R = Pr^n, Bu^n)[13] which were obtained from $RuCl_3$ and the appropriate ligand. A good source for the synthesis of ruthenium(III) complexes is $RuX_3(EPh_3)_2(MeOH)$ (X = Cl or Br; E = P or As)[1,9] which reacts with various ligands to yield mixed ligand complexes that could not be obtained directly from ruthenium trichloride. Depending on the type of ligand used, complexes of ruthenium(III) or (II) can be obtained.[14,15]

In view of the growing importance of ruthenium complexes as catalysts in a variety of reactions,[16] it was considered necessary to search for new, convenient and single-stage synthetic routes for the preparation of these compounds. The present paper deals with the syntheses of some ruthenium(II) and (III) complexes involving monotertiary phosphines and arsines. By suitable variation of the solvent and temperature, methods were developed to obtain a particular geometrical form of the phosphine or arsine complexes.

EXPERIMENTAL

Ruthenium trichloride trihydrate and the ligands used in this work were obtained as reported earlier.[17] The complexes $RuCl_2(PPh_3)_3$ and $RuCl_3(AsPh_3)_2(MeOH)$ were prepared by published procedures.[1] Dried, degassed reagent grade solvents were used in all preparations, which were carried out in an atmosphere of dry nitrogen. Microanalyses, melting points, conductivity measurements were done as reported[17a]. Magnetic susceptibility measurements at room temperature were done on a Faraday Balance. NMR data were recorded on a HA-100 MHz spectrometer in $CDCl_3$.

Microanalytical data, conductivity, melting points and magnetic susceptibility data are presented in Table I. The electronic spectral results are presented in Table III.

Preparation of complexes

1) *cis-Dichlorotetrakis(methyldiphenylarsine)ruthenium(II)* The complex $RuCl_2(PPh_3)_3$ (0.20 gm, 0.2 mM) was suspended in degassed petroleum ether (b.p. 60–80°) and heated under reflux for fifteen minutes. A solution of methyldiphenyl-arsine (0.30 gm, 1.25 mM) in the same solvent was added to the above solution. After the addition of the ligand the suspension of the complex dissolved giving a yellow-brown solution. The solution was refluxed for a further six hours in an atmosphere of nitrogen, and evaporated to half its volume, cooled overnight, when a dirty yellow product precipitated. The complex was filtered and washed with light petroleum ether (b.p. 40–60°) to remove the excess of arsine and the dissociated phosphine and finally dried over P_2O_5 in vacuum. Yield: 0.13 gm (72%). Recrystallised from dichloromethane and *n*-hexane.

2) *cis-Dichlorotetrakis(dimethylphenylarsine)ruthenium(II)* A solution of dimethylphenylarsine (0.22 gm, 1.25 mM) in petroleum ether (b.p. 60–80°) was added to the suspension of $RuCl_2(PPh_3)_3$ (0.20 gm, 0.2 mM) in the same solvent under reflux in an atmosphere of nitrogen. As soon as the ligand was added the whole suspension dissolved giving a homogeneous yellow solution. The reaction mixture was further refluxed for an hour when orange coloured crystals started settling on the walls of the reaction flask. The crystals were filtered and collected after several washings with light petroleum ether (b.p. 40–60°). Yield: 0.14 gm (95%). Recrystallized from dichloromethane and n-hexane.

N.B:–The dissociated triphenylphosphine from the filtrate was isolated and recrystallized. (Tested by IR and melting point.)

3) *trans-Dichlorotetrakis(dimethylphenylarsine)ruthenium(II)* The complex $RuCl_3(AsPh_3)_2(MeOH)$ (0.20 gm, 0.23 mM) dissolved in benzene and dimethylphenylarsine 0.25 gm, 1.40 mM) in methanol were refluxed in the presence of zinc-amalgam in a nitro-

TABLE I

Analytical and other data for Ruthenium(II) and (III) complexes

Sl. No.	Complex	Colour	Magnetism μ_{eff} (B.M.)	M.P.[b] (°C)	Analysis %[a] C	Analysis %[a] H	Analysis %[a] Cl	Conductivity[c] (ohm^{-1} cm^2 equiv^{-1})
1	*cis*-$RuCl_2(AsMePh_2)_4$	Dirty yellow	Diamag	122–124	55.41 (54.35)	4.47 (4.52)	6.00 (6.18)	23.53
2	*cis*-$RuCl_2(AsMe_2Ph)_4$	Orange yellow	Diamag	198	43.10 (42.66)	4.98 (4.89)	8.00 (7.88)	26.55
3	*trans*-$RuCl_2(AsMe_2Ph)_4$	Red	Diamag	191–193	42.69 (42.66)	5.05 (4.89)	7.50 (7.88)	—
4	*mer*-$RuCl_3(PPh_3)_3$	Brown	2.04	138–141	64.66 (65.20)	4.44 (4.53)	—	23.03
5	*mer*-$RuCl_3(PMePh_2)_3$	Greenish yellow	1.98	200	54.86 (57.94)	4.94 (4.82)	—	33.60
6	*mer*-$RuCl_3(PMe_2Ph)_3$	Brown	1.86	130	45.38 (46.30)	5.20 (5.30)	—	40.62
7	*mer*-$RuCl_3(PEtPh_2)_3$	Orange yellow	2.12	155–157	57.99 (59.32)	5.12 (5.19)	—	34.82
8	$RuCl_2(PMePh_2)_3$	Yellow	Diamag	183–190	60.38 (60.62)	5.18 (5.05)	9.10 (9.19)	16.14
9	$[RuCl_2(AsPh_3)_2]_n$	Dark brown	—	193–198	53.50 (55.10)	3.87 (3.82)	—	—
10	$[RuCl_2(PPh_3)(AsPh_3)]_n$	Brown	—	218–222	57.33 (58.30)	4.24 (4.05)	—	—

[a] Calculated values in parentheses; [b] Decomposition temperatures; [c] Measured in DMA.

TABLE II
Infrared spectra of Ruthenium(II) and (III) complexes (100–650 cm^{-1})

Sl. No.	Complex	ν(Ru-Y) (cm^{-1}) (Y = P, As)	ν(Ru-Cl) (cm^{-1})	Other ligational bands
1	*cis*-$RuCl_2(AsMePh_2)_4$	480(vs)	312(s), 270(s)	630(m), 605(s), 340(m)
2	*cis*-$RuCl_2(AsMe_2Ph)_4$	476(vs)	305(s), 275(s)	600(s), 380(w), 300(s), 278(m), 258(w), 223(s), 162(w)
3	*trans*-$RuCl_2(AsMe_2Ph)_4$	475(vs)	308(vs)	595(s), 590(s), 550(w), 395(w), 388(w), 255(w), 160(b, m)
4	*mer*-$RuCl_3(PPh_3)_3$	540(vs)	360(m), 335(s), 290(s)	620(m), 522(sh), 465(vw)
5	*mer*-$RuCl_3(PMePh_2)_3$	514(vs)	365(m), 310(m), 273(s)	498(m), 400(m), 158(w)
6	*mer*-$RuCl_3(PMe_2Ph)_3$	568(m)	330(s), 270(w), 240(w)	492(s), 425(m), 164(w)
7	*mer*-$RuCl_3(PEtPh_2)_3$	515(vs)	361(m), 310(s), 283(m)	488(s), 460(w), 445(m), 420(s), 140(m)
8	$RuCl_2(PMePh_2)_3$	514(vs)	360(b, m), 283(m)	570(w), 492(sh), 450(s), 410(s), 312(w)
9	$[RuCl_2(AsPh_3)_2]_n$	470(vs), 475(vs)	280(s), 265(s)	330(s)
10	$[RuCl_2(PPh_3)(AsPh_3)]_n$	525(vs), 475(vs)	330(vs), 275(s), 245(w)	620(m), 540(s), 490(w), 425(m), 390(vw), 320(sh)

Key: s = strong; vs = very strong; sh = shoulder; w = weak; vw = very weak; m = medium; b = broad.

TABLE III
Electronic spectral results of Ruthenium(II) and (III) complexes in the range 1000–200 nm in methanol and their probable assignments

Complex	Absorption maxima		ε	Assignment
	nm	cm^{-1}	(M^{-1} cm^{-1})	
1) *cis*-RuCl$_2$(AsMePh$_2$)$_4$	615	16260	669	d — d
	400	25000	1458	
	340	29411	2215	
	272	36764	8443	$\pi \rightarrow \pi^*$
	265	37735	11820	
	220	45454	59946	M → L or L → M
2) *cis*-RuCl$_2$(AsMe$_2$Ph)$_4$	610	16393	72	d — d
	500	20000	638	
	295	33898	9447	
3) *trans*-RuCl$_2$(AsMe$_2$Ph)$_4$[a]	975	10256	3	d — d
	900	11111	5	
	612	16339	62	
	502	19920	751	
	428	23364	379	
4) *mer*-RuCl$_3$(PPh$_3$)$_3$	610	16393	297	d — d
	400	25000	1143	
	340	29411	1818	
	272	36764	4290	$\pi \rightarrow \pi^*$
	265	37735	3716	
	258	38759	2001	
	251	39840	1429	
	225	44444	61749	M → L or L → M
5) *mer*-RuCl$_3$(PMePh$_2$)$_3$	600	16666	266	d — d
	385	25974	1789	
	330	30303	2490	
	272	36764	4836	$\pi \rightarrow \pi^*$
	264	37878	6045	
	258	38759	8705	
	250	40000	11606	Charge transfer involving P lone pair and benzene ring (n → π^*)
	246	40650	13540	
	225	44444	35061	M → L or L → M
6) *mer*-RuCl$_3$(PMe$_2$Ph)$_3$	615	16260	247	d — d
	390	25641	1306	
	335	29850	2590	
	269	37174	6081	$\pi \rightarrow \pi^*$
	263	38022	7657	
	235	42553	20945	$\pi \rightarrow \pi^*$ (intraligand)
	218	45871	35810	M → L or L → M

TABLE III—*continued*

Complex	Absorption maxima		ε	Assignment
	nm	cm^{-1}	$(M^{-1}\,cm^{-1})$	
7) mer-$RuCl_3(PEtPh)_3$	610	16393	238	d — d
	390	25641	1536	
	335	29850	2039	
	272	36764	2648	$\pi \rightarrow \pi^*$
	266	37593	2648	
	264	37878	2648	
	259	38610	4237	
	250	40000	6621	$\pi \rightarrow \pi^*$ (intraligand)
	245	40816	7945	
	225	44444	24631	M → L or L → M
8) $RuCl_2(PMePh_2)_3$[a]	972	10288	10	Spin-forbidden
	895	11173	13	
	695	14388	8	
	400	25000	950	d — d
	356	28089	1494	
	300	33333	2961	

[a]The spectra were measured in chloroform.

gen atmosphere for three hours. The ratio of methanol to benzene was approximately 1 : 1. The red solution was filtered and cooled at room temperature for 24 hours, when red needle like crystals separated. These crystals were collected by filtration, washed with n-hexane and dried in vacuum. The complex was recrystallized from dichloromethane and methanol (1:4 mixture) to yield red needles. Yield: 0.14 gm (83%).

4) *mer-Trichlorotris(triphenylphosphine)ruthenium(III);*
5) *mer-Trichlorotris(methyldiphenylphosphine)ruthenium(III);*
6) *mer-Trichlorotris(dimethylphenylphosphine)ruthenium(III);*
7) *mer-Trichlorotris(ethyldiphenylphosphine)ruthenium(III)* These complexes were prepared by the addition of 4 mM excess each of PPh_3, $PMePh_2$, PMe_2Ph and $PEtPh_2$ respectively in benzene to 1 mM of $RuCl_3(AsPh_3)_2(MeOH)$ in 40 ml of the same solvent and refluxing for four hours. The colour of the solution remained brown in the case of PPh_3 and PMe_2Ph. In the case of $PMePh_2$ and $PEtPh_2$ the initial colour changed from yellow-brown to yellow and green, respectively. The solutions were evaporated to a small volume under vacuum and the products precipitated with petroleum ether (60–80°). The products were washed repeatedly with petroleum ether (60–80°) and dried in vacuum. The complexes were recrystallized from dichloromethane and n-hexane to give $RuCl_3L_3$ ($L = PPh_3$, $PMePh_2$, PMe_2Ph and $PEtPh_2$).

8) *Dichlorotris(methyldiphenylphosphine)ruthenium(II)* The complex $RuCl_3(AsPh_3)_2$-(MeOH)(0.20 gm, 0.23 mM) was refluxed with 10 moles excess of methyldiphenylphosphine (0.47 gm, 2.35 mM) in benzene for 5 hours in an atmosphere of nitrogen. During the course of the reaction the solution remained greenish yellow. The solution was evaporated to small volume and the complex precipitated with methanol when a yellow mass

separated. The complex was washed with cold methanol and *n*-hexane and dried *in vacuo*. Yellow crystals of the complex were obtained on recrystallizing from dichloromethane/petroleum ether (60–80°) or a dichloromethane-*n*-hexane mixture. Yield: 0.15 gm (83%).

9) $[RuCl_2(AsPh_3)_2]_n$ To a suspension of $RuCl_3(AsPh_3)_2(MeOH)$ (0.20 gm, 0.23 mM) in propanol, $AsPh_3$ (0.30 gm, 0.98 mM) dissolved in the same solvent was added, when the whole reaction mixture became a homogeneous solution after five minutes of refluxing. This was further refluxed for five hours, when brown crystals separated out. They were filtered, washed to remove excess of arsine with petroleum ether (60–80°) and dried in air. Yield: 0.13 gm (80%).

10) $[RuCl_2(AsPh_3)(PPh_3)]_n$ Ruthenium trichloride trihydrate (0.20 gm, 0.76 mM) dissolved in propan-1-ol was refluxed for five hours with PPh_3 (0.60 gm, 2.3 mM) in an atmosphere of nitrogen. At this stage the separation of the phosphine complex was complete. The complex was refluxed with $AsPh_3$ (0.70 gm, 2.3 mM) in propan-1-ol for twelve hours, when a deep-brown crystalline complex separated. The complex was filtered, washed with diethyl ether and dried in vacuum. Yield: 0.53 gm (94%).

RESULTS AND DISCUSSION

Three types of starting materials, $RuCl_3.3H_2O$, $RuCl_2(PPh_3)_3$ and $RuCl_3(AsPh_3)_2(MeOH)$ were employed in the present investigation for the synthesis of ruthenium(II) and ruthenium(III) complexes. From a preparative view point the latter two sources offer lot of advantages over the former. The complex $RuCl_2(PPh_3)_3$ is particularly suitable as a convenient starting material for the preparation of ruthenium(II) complexes. The complexes *cis*-$RuCl_2(AsMePh_2)_4$(*1*) and *cis*-$RuCl_2(AsMe_2Ph)_4$(*2*) were obtained by the complete displacement of triphenylphosphine from the complex $RuCl_2(PPh_3)_3$ in a non-polar solvent like petroleum ether (60–80°) using an excess of the arsine ligand. The displacement was found to be very rapid in the case of basic arsines and follows the order $AsMe_2Ph > AsMePh_2$. Triphenylarsine, which is much less basic than the other two arsines, failed to displace triphenylphosphine even after 100 hours of reaction. This indicates that PPh_3 is more strongly bound to the metal ion than $AsPh_3$ as expected from the π-acidity of the two ligands; the former is a better π-acid compared with the latter. The triphenylphosphine displacement reaction from $RuCl_2(PPh_3)_3$ with other phosphines more often than not yields dimeric products.[18] The displacement reaction with arsines however yields predominantly neutral monomeric products and thus offers an advantage as a preparative method over the former reaction.

Complex *1* was obtained earlier by Nyholm *et al*[4] by a two-step method involving the preparation of $RuCl_3(AsMePh_2)_3$ and reduction of the same by H_3PO_2 in alcohol. In the present investigation a one-step synthesis of complex *1* has been achieved in much better yields than the earlier method.[4] The complexes *cis*-and *trans*-$RuCl_2(AsMe_2Ph)_4$(*2* and *3* respectively) were earlier reported in a single preparation by Chatt *et al*[3] by a route involving the refluxing of a solution of ruthenium-trichloride trihydrate and dimethylphenylarsine in methanol for 17 hours. In the present work complexes *2* and *3* were prepared in a pure form and good yields by independent routes, The reaction time is also reduced to a few hours. The complex *trans*-$RuCl_2(AsMe_2Ph)_4$(*3*) was prepared from the complex $RuCl_3(AsPh_3)_2(MeOH)$ by the displacement of $AsPh_3$ by $AsMe_2Ph$ and the reduction of ruthenium(III) to ruthenium(II) complex by zinc-amalgam in a 1 : 1 mixture of benzene-methanol.

The infrared spectra of complexes *1*–*3* display the usual bands corresponding to the ligational modes of $AsMePh_2$ and $AsMe_2Ph$ respectively (Table II). The complexes display very strong bands in the range 470–480 cm^{-1} due to Ru-As stretching modes. The spectra of *1* and *2* show no bands around 520 cm^{-1} which could be assigned to Ru-P stretching modes confirming the complete displacement of phosphine from the coordination sphere of the metal ion. The Ru-Cl stretching frequencies at 312 and 270 cm^{-1} in complex *1* and at 305 and 275 cm^{-1} in complex *2* are indicative of *cis*-disposition of chloro ligands, since the *trans* complex will give only one peak. A single strong peak at 308 cm^{-1} in complex *3* suggests *trans*-chlorides in the complex.

The ^1H NMR spectra of the methyl protons in complexes *2* and *3* are very well resolved and support the assigned configurations. The methyl protons of the *cis*-complex *2* are observed as two singlets of 1 : 1 intensity at 8.54 τ and 8.84 τ, respectively. The phenyl-protons of the *cis*-dimethylphenylarsine ligands merge to give a broad and not so clearly resolved multiplet centred at 2.70 τ.

The ^1H NMR spectrum of complex *3* shows a singlet at 8.54 τ corresponding to the methyl protons of the dimethylphenylarsine ligand. In this case the phenyl protons of the *trans*-disposed arsine ligands are very well resolved and appear as two multiplets at 2.30 τ and 2.74 τ in the ratio of 1 : 1. The integration of phenyl to methyl protons in the complex are in the ratio of 5 : 6. The phenyl proton resonance is split into a multiplet by the non-equatorial methyl protons of dimethylphenylarsine. The split into two multiplets may be due to a slight distortion from planarity of the plane containing the arsine ligands. Complexes *1*–*3* are diamagnetic corresponding to a spin-paired t_{2g}^6 configuration of ruthenium(II).

Complexes of the type *mer*-$RuCl_3L_3$ (L = PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$) (*4*–*7*) were prepared from $RuCl_3(AsPh_3)_2(MeOH)$ by the displacement of arsine and methanol with the appropriate phosphine ligands in the mole ratio of 1:4 in boiling benzene. No reaction took place when the same displacement was attempted in non-polar solvents like petroleum ether or n-hexane. Complexes *4* and *6* were earlier reported by Chatt *et al*[8] by the direct interaction of ruthenium trichloride trihydrate with the appropriate phosphine ligand in strongly acidified ethanol. In the present work complexes *4*–*7* were obtained by a facile displacement of triphenylarsine from $RuCl_3(AsPh_3)_2(MeOH)$ by an excess (1 : 4) of phosphine ligand. The arsine ligand is completely displaced from $RuCl_3(AsPh_3)_2(MeOH)$ by the more basic phosphines with no reduction in the oxidation state of the metal ion. The complete displacement of arsine in the complexes is confirmed by the absence of a peak due to the coordinated arsine in the infrared spectra of these complexes (Table II). Complexes *4*–*7* are paramagnetic corresponding to one unpaired electron (Table I) characteristic of a low-spin $4d^5$ configuration of the ruthenium(III) complexes.

Complexes of the type MX_3L_3 may exist in two geometric isomers: facial and meridonial. The far-IR spectra of the two isomers are expected to be quite distinct with three infrared active metal-halogen (M-X) stretching vibrations in the *mer*-isomers but only two in the fac-isomers.[19] The spectra taken in solid state generally conform to this pattern, but some *mer*-isomers of iridium complexes[20] have shown exceptions to the above rule in that they exhibit two rather than three bands. This behaviour was attributed to a low transition moment associated with $\nu(M\text{-}X_3)$ $a_1(2)$ vibrations[20]. Another exception to this rule is mer-$RuBr_3(PMe_2Ph)_3$ which shows four bands due to Ru-Br stretching vibrational modes.[21] Complexes *4*–*7* display three bands in each case corresponding to ν(Ru-Cl) (Table II) which can be assigned to a meridonial configuration of the complexes. There are also intense bands at 540, 514, 568 and 515 cm^{-1} respectively in complexes *4*–*7* which can be assigned to ν(Ru-P) vibrational modes.

^1H NMR may also be used to distinguish between the *mer*- and *fac*-configurations. For complexes *4*–*7*, however, good resolved NMR spectra could not be obtained as these complexes possess a paramagnetic Ru(III) ion as evidenced by magnetic susceptibility measurements at room temperature (Table I). Paramagnetic complexes always give much broader NMR spectral absorptions compared to their diamagnetic analogues and these are also shifted by contact and pseudo-contact mechanisms.[21] However it has been reported that in the case of the complex $RuCl_3(PMe_2Ph)_3$ the spectrum had enough details to suggest a meridonial configuration.[22]

An attempt to carry out the reduction of the complex $RuCl_3(AsPh_3)_2(MeOH)$ in benzene with an excess of methyldiphenylphosphine resulted in the formation of the ruthenium(II) complex, $RuCl_2(PMePh_2)_3$(*8*). Under the same set of reaction conditions the amount of the ligand seems to control the nature of the product: substitution without reduction or with reduction. Earlier studies[18] on the ligand-exchange reactions involving various phosphines were shown to be sensitive both to the nature of the solvent and to the phosphine used. The complex $RuCl_2(PMePh_2)_4$ obtained from ligand exchange reactions[18] was reported to undergo rearrangement in solution to give an ionic species $[Ru_2Cl_3(PMePh_2)_6]Cl$. In the presence of 4 moles excess of various phosphines (e.g. PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$) in benzene, ruthenium(III) complexes of the type $RuCl_3L_3$(*4–7*) were obtained from $RuCl_3(AsPh_3)_2(MeOH)$. In the presence of excess phosphine (ten moles excess) complex $RuCl_2(PMePh_2)_3$(*8*) was obtained. Complex *8* was obtained as a yellow compound soluble in most organic solvents. This appears to be the first report of a penta-coordinate complex of ruthenium(II) containing methyldiphenylphosphine although a few complexes of ruthenium(II) with other phosphines[1,18] and triphenylstibine[1] are known, and the structure of $RuCl_2(PPh_3)_3$ is reported.[23] The solution of complex *8* in DMA is initially non-conducting ($\lambda_\infty = 16.14\ ohm^{-1}\ cm^2\ equiv^{-1}$). However, on standing for prolonged periods the DMA solution of the complex conducts and the increase in conductivity was gradual, suggesting the formation of the ionic species $[Ru_2Cl_3(PMePh_2)_6]Cl$ as reported by Stephenson and coworkers.[18]

The far-IR spectrum of complex *8* shows bands at 360 and 283 cm^{-1} due to Ru-Cl stretching modes indicating a *cis*-disposition of chlorides in the complex. The IR spectrum of complex also displays a strong band at 514 cm^{-1} due to coordinated phosphine. The ^1H NMR spectrum of this complex shows methyl resonance signals at 6.43 τ and 7.98 τ in the ratio of 1 : 2 and a phenyl multiplet at 2.76 τ. The ^1H NMR spectrum thus supports either a trigonal bipyramid structure with *cis-cis-trans* arrangement of phosphines and a *cis*-arrangement of chlorides, or a square pyramidal configuration with a basal disposition of phosphines and *cis*-chlorides. The corresponding complex $RuCl_2(PPh_3)_3$ has the latter configuration[23]. Both the configurations, trigonal bipyramid (C_{2V}) and square pyramid (with a local C_s symmetry) are equally probable and account for the diamagnetism of the complex. Steric considerations however favour the square pyramidal geometry with a meridonial arrangement of phosphines.

Ligand displacement reactions on the complex $RuCl_3(AsPh_3)_2$ (MeOH) were conducted both in polar and non-polar solvents with a variation in boiling points at reflux temperatures. The reaction of the complex with various phosphines in non-polar solvents like benzene gave monomeric neutral ruthenium(II) or (III) complexes. When reaction of this complex with one mole excess triphenylarsine was carried out in propan-1-ol at 101°C, a polymer $[RuCl_2(AsPh_3)_2]_n$ was obtained. Thus higher boiling solvents promote the polymerization of the complex. Owing to the insolubility of *9* in all common organic solvents it was not possible to characterise it by physico-chemical methods. The far-IR spectrum of the complex displays strong bands at 470 and 475 cm^{-1} due to the coordinated arsine and at 280 and 265 cm^{-1} due to the bridging chlorides.

The reaction of $RuCl_3.3H_2O$ in propan-1-ol with triphenylarsine and triphenylphosphine was carried out in order to prepare mixed ligand complexes containing both the ligands. The method however yielded a polymeric ruthenium(II) mixed ligand complex $[RuCl_2(PPh_3)(AsPh_3)]_n$(*10*). Complex *10* is insoluble in most common organic solvents. The presence of both the phosphine and arsine in the coordination sphere of the metal ion is confirmed by the presence of strong bands in the IR spectrum at 525 and 475 cm^{-1} attributable to the Ru-P and Ru-As stretching modes respectively. An intense band at 275 cm^{-1} and a weak band at 245 cm^{-1} are assigned to Ru-Cl-Ru modes.

Complexes *9* and *10* produce brown and green solutions on prolonged dissolution (for a period of 24 hours) in DMA and DMF respectively. These solutions in DMA have shown considerable conductivity suggesting the formation of ionic polymers of unknown composition. The isolation and identification of these species was not successful.

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