RUTHENIUM(II) COMPLEXES WITH TRIPHENYLPHOSPHINE OR TRIPHENYLARSINE AND OTHER MONODENTATE LIGANDS

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Abstract—Synthesis and studies on some five-coordinate ruthenium(II) complexes, viz. $[Ru(MPh_3)(C_6H_5CHO)_2Cl_2]$ and $[Ru(MPh_3)_2(CO)Cl_2]$ (where M = P or As) have been described. Reactions of $[Ru(MPh_3)(C_6H_5CHO)_2Cl_2]$ with N,N-dimethylformamide, dimethylsulphoxide and pyridine and of $[Ru(MPh_3)_2(CO)Cl_2]$ with pyridine are described.

The chemistry of the complexes of ruthenium(II) and ruthenium(III) containing strong donor ligands such as mono-tertiary-phosphine, arsine or stibine has been studied extensively.¹⁻²³ The chemistry of the complexes of ruthenium(II) and ruthenium(III) with relatively weak donor ligands, such as dimethylsulphoxide, pyridine and acetonitrile has been studied.24–28 relatively less Complexes of ruthenium(II) and ruthenium(III) containing both strong and weak donor ligands where the coordination around metal ion is generally six have also been studied in detail.^{2,9,13,19,21,22,29-37} Complexes of ruthenium(II) containing weak donor ligands or having both strong and weak donor ligands have a strong potential to act as catalysts in various homogeneous reactions.²⁴

Most of the complexes of ruthenium(II) and ruthenium(III) of the type discussed above involve six coordinated metal ions. Complexes having pentacoordination have a strong potential to act as catalysts in various homogeneous reactions. Here, some pentacoordinated complexes of ruthenium(II) containing triphenylphosphine or triphenylarsine and benzaldehyde are reported. Some of their reactions to substitute the coordinated benzaldehyde by weak donor ligands are also described.

EXPERIMENTAL

All the chemicals used were reagent grade. Ruthenium trichloride hydrate was supplied by

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Aurora-Matthey Limited, Calcutta.

 $[\operatorname{RuCl}_2(\operatorname{PPh}_3)_2]_n^{20}$ $[\operatorname{RuCl}_2(\operatorname{PPh}_3)_3]^2$

and

 $[RuCl_2(AsPh_3)_2]_2^{20}$

were prepared according to reported methods.

Preparations

 $[RuCl_2(MPh_3)(C_6H_5CHO)_2]$ (M = P or As). To solution of ruthenium trichloride hydrate a $(RuCl_3 \cdot xH_2O)$ (0.1 g) in *n*-butanol (10 cm³), benzaldehyde (2 cm³) was added. A solution of triphenylphosphine (0.5 g) or triphenylarsine (0.6 g)in *n*-butanol (5 cm^3) was added to the hot solution of ruthenium trichloride mentioned above. The resulting solution was then refluxed for about 30 min or 2 h, in the case of triphenylphosphine or triphenylarsine respectively. The reaction mixture was cooled overnight when a brownish-yellow crystalline compound in the case of triphenylarsine and a light green compound in the case of triphenylphosphine was obtained. The compound was separated by centrifugation and washed first with methanol and then with diethylether and dried under vacuum. The compounds were analysed for $[RuCl_2(MPh_3)(C_6H_5CHO)_2].$

 $[RuCl_2(CO)(AsPh_3)_2]$. (i) To a clear solution of ruthenium trichloride hydrate (0.1 g) in *n*-butanol (10 cm³) and benzaldehyde (2 cm³) mixture, a solution of triphenylarsine (1 g) in *n*-butanol (5 cm³) was added

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and the mixture was refluxed for about 20 h. Initially, benzaldehyde complex was formed which went into solution and finally an orange solution was obtained which on cooling yielded a yellow compound. The mother liquor upon concentration under reduced pressure and cooling yielded more of the yellow compound, which was centrifuged, washed first with acetone and then with ether and dried under vacuum. It was analysed for [Ru(CO)(AsPh₃)₂Cl₂].

(ii) $[RuCl_2(CO)(AsPh_3)_2]$ could be obtained also by boiling under reflux $[RuCl_2(AsPh_3)_2]_2$ (0.2 g) in benzaldehyde (2 cm³) and *n*-butanol (10 cm³) mixture for about 8 h or by boiling under reflux $[RuCl_2(C_6H_5CHO)_2(AsPh_3)]$ (0.2 g) and triphenylarsine (0.2 g) in *n*-butanol (10 cm³) for about 10 h and cooling the orange-red solution obtained.

 $[\operatorname{RuCl}_2(\operatorname{CO})(\operatorname{PPh}_3)_2]$ (reddish-brown). To a solution of ruthenium trichloride hydrated (0.2 g) in *n*-butanol (20 cm³) and benzaldehyde (4 cm³) mixture, a solution of triphenylphosphine (1.5 g) in *n*-butanol (10 cm³) was added and the mixture was boiled under reflux for 6–8 h, when a reddish-brown crystalline compound (m.p. 195–200°C) separated out which was separated by centrifugation and washed first with methanol and then with diethylether and dried under vacuum. It was analysed for [RuCl₂(CO)(PPh₃)₂].

 $[RuCl_2(CO)(PPh_3)_2](yellow).$ (i) The reaction was carried out in a way similar to that for the reddish-

brown compound mentioned above, except that the reaction mixture was refluxed for 15-20 h, when the red crystalline compound obtained as an intermediate went into solution and finally a reddish-yellow solution was obtained, which on cooling resulted in the separation of a yellow compound. The compound was separated and washed first with acetone and then with ether. Concentration of the mother liquor resulted in the separation of more yellow compound. The compound was analysed for [RuCl₂(CO)(PPh₃)₂].

(ii) The yellow compound could also be obtained by boiling under reflux $[RuCl_2(PPh_3)_2]_n$ or $[RuCl_2(PPh_3)_3]$ (0.2 g) in benzaldehyde (2 cm³) and *n*-butanol (10 cm³) mixture for about 8 h or by boiling under reflux $[RuCl_2(C_6H_5CHO)_2(PPh_3)]$ (0.2 g) and triphenylphosphine (0.2 g) in *n*-butanol (10 cm³) for about 10 h and cooling the reddishyellow solution obtained.

Reactions of $[Ru(MPh_3)(C_6H_5CHO)_2Cl_2]$ (M = P, or As) with L = pyridine, N,N-dimethylformamide (DMF) and dimethylsulphoxide (DMSO). [Ru(MPh_3)(C_6H_5CHO)_2Cl_2] (0.2 g) was taken with L (0.5 cm³) and heated on a water-bath for about 1 h, when a clear solution was obtained. To the cold solution, methanol was added in the case of DMF or DMSO and the diethylether in the case of pyridine reaction and the mixture was kept overnight when crystalline compound separated out. It

Compound	Colour	m.p. °C	% C (calc.)	% H (calc.)	% N (calc.)	% Cl (calc.)
$[Ru(AsPh_3)(benz)_2Cl_2]$	Brownish-	188–192	55.28	3.94	_	10.15
	yellow		(55.65)	(3.91)		(10.29)
[Ru(PPh ₃ (benz) ₂ Cl ₂]	Light-	175–182	59.21	4.44		10.73
	green		(59.44)	(4.18)		(10.99)
$[Ru(CO)(PPh_3)_2Cl_2]$	Reddish- brown	195–200	61.60	4.32	_	10.00
			(61.32)	(4.14)		(9.81)
$[Ru(CO)(AsPh_3)_2Cl_2]$	Yellow	260-267	54.92	3.85	_	8.38
			(54.68)	(3.69)		(8.74)
[Ru(CO)(PPh ₃) ₂ Cl ₂]	Yellow	270–275	61.49	4.36	_	10.05
			(61.32)	(4.14)		(9.81)
[Ru(AsPh ₃)(py) ₃ Cl ₂]	Reddish- brown	198–200	54.95	3.95	6.12	9.62
			(55.38)	(4.20)	(5.87)	(9.93)
[Ru(AsPh ₃)(DMF) ₃ Cl ₂]	Reddish- brown	205–210	46.05	4.69	6.41	9.76
			(46.48)	(5.16)	(6.03)	(10.19)
[Ru(PPh ₃)(DMF) ₃ Cl ₂]	Yellowish- brown	215-220	50.06	5.12	6.11	11.24
			(49.62)	(5.51)	(6.43)	(10.87)
[Ru(CO)(py) ₂ (AsPh ₃)Cl ₂]	Yellow	208–210	52.73	3.42	4.54	11.12
			(52.41)	(3.77)	(4.22)	(10.69)
$[Ru(CO)(py)_2(PPh_3)Cl_2]$	Yellow	180-185	55.67	3.86	4.28	11.69
			(56.13)	(4.03)	(4.52)	(11.45)

Table 1. Some physical and analytical data of new ruthenium(II) complexes

benz = benzaldehyde; py = pyridine.

Compound	Electronic spectral bands : λ_{max} in nm (ε_{max})	Important IR absorptions in cm ⁻¹
[Ru(AsPh ₃)(benz) ₂ Cl ₂]	810 (220) 520 sh 410 (1460)	1615 m 1595 m 1575 m 1450 m 1218 m 670 m 330 s
[Ru(PPh ₃)(benz) ₂ Cl ₂]	765 (225) 420 (1500)	1615 m 1597 m 1580 m 1452 m 1220 m 675 m
[Ru(AsPh ₃)(py) ₃ Cl ₂]	450 (1105) 390 (2300)	1445 m
[Ru(AsPh ₃)(DMF) ₃ Cl ₂]	510 (250) 405 (1050)	1640 s 1360 m
[Ru(PPh ₃)(DMF) ₃ Cl ₂]	550 (240) 415 (1250)	1642 s 1358 m
[Ru(CO)(py) ₂ (PPh ₃)Cl ₂]	_	1962 m–s 1945 m–s 1442 m
[Ru(CO)(py) ₂ (AsPh ₃)Cl ₂]	. –	1952 m 1940 s 1923 m 1445 m

 Table 2. Electronic absorption and important IR spectral data of ruthenium(II) complexes

benz = benzaldehyde; py = pyridine; DMF = dimethylformamide.

was centrifuged, washed with ether and dried under vacuum. The compounds obtained had the composition $[RuCl_2(MPh_3)L_3]$ (where M =P or As and L = pyridine or DMF) and $[RuCl_2(DMSO)_4]$.

Reaction of $[Ru(MPh_3)_2(CO)Cl_2]$ with pyridine. $[Ru(MPh_3)_2(CO)Cl_2]$ (M = P or As) (0.2 g) was taken with pyridine (1 cm³) and heated on a water bath when a clear yellow solution was obtained. After cooling the solution, ether was added when yellow compound precipitated out, which was centrifuged, washed with ether and dried under vacuum. The compounds had the composition $[RuCl_2(CO)(MPh_3)(py)_2].$

Carbon, hydrogen and nitrogen analyses were obtained from the Microanalytical Laboratory, I.I.T., Kanpur. Chloride estimations were carried out according to standard methods³⁸ gravimetrically after decomposing the complexes using KNO₃, KOH mixture. IR spectra were recorded in KBr as pellets in the region 4000-600 cm⁻¹ on a Perkin-Elmer 297 IR spectrophotometer, and on Perkin-Elmer 580 spectrophotometer in the region 600-250 cm^{-1} for some complexes. Visible electronic spectra were recorded in chloroform in the region 800-350 nm on a Beckmann-26 spectrophorometer. Proton magnetic resonance spectra were recorded on a Varian EM-390, 90 MHz spectrometer in CDCl₃, with TMS as reference. Magnetic susceptibility measurements were carried out using a Gouy balance at room temperature. Mercurv tetrathiocyanatocobaltate(II) was used as calibrant. All the melting points are uncorrected. The conductivity measurements were made using an Elico type CM 82 conductivity bridge in nitrobenzene.

RESULTS AND DISCUSSION

(a) $[Ru(MPh_3)(C_6H_5CHO)_2Cl_2] (M = P \text{ or } As)$

Ruthenium compounds containing triphenylphosphine or triphenylarsine and benzaldehyde have the composition $[Ru(MPh_3)(C_6H_5CHO)_2Cl_2]$ (M = P or As). Benzaldehyde is easily oxidised to benzoic acid. As the reactions were carried out in the presence of air, the possibility of benzaldehyde getting oxidised to benzoic acid and coordinating to the ruthenium can not be eliminated. However, a similar reaction under nitrogen atmosphere also gave the same products. The PMR of $[Ru(AsPh_3)(C_6H_5CHO)_2Cl_2]$ in dueterated chloroform showed signals at 10, 7.31 and 7.23 δ . The signals at 10 and at 7.31 and 7.32 δ were in the ratio 2:25. The aryl aldehyde proton is normally observed in the 10.1–9.5 δ range.³⁹ In the benzaldehyde complex containing triphenylarsine, a proton signal at 10δ can unambiguously be assigned as due to the proton of the aldehyde functional group of benzaldehyde. The signals at 7.31 and 7.23 δ are due to the phenyl groups of triphenylarsine and benzaldehyde respectively. The ratio of the proton signals for aldehydic proton and the phenyl protons is as expected (2:25). Similarly, the triphenylphosphine analogue, viz. [Ru(PPh₃)(C₆H₅CHO)₂Cl₂], gave proton signals at 10, 7.5 and 7.23 δ . The ratio of 10δ to 7.5 and 7.23 δ signals is again 2:25 as expected for two aldehyde protons and 25 phenyl protons. The signals at 7.5 and 7.23 δ are due to the phenyl groups of triphenylphosphine and benzaldehyde respectively. Thus, the PMR spectra of $[Ru(MPh_3)(C_6H_5CHO)_2Cl_2]$ (M = P or As) confirmed the presence of three phenyl groups due to triphenylphosphine or arsine, two phenyl groups and two aldehydic protons due to two benzaldehyde molecules.

The IR spectra of the two complexes discussed above showed all the bands due to triphenylphosphine or triphenylarsine and benzaldehyde. Among the important IR bands due to benzaldehyde are three bands of medium intensity at 1615, 1595 and 1575 cm^{-1} and bands at 1450, 1220 and 670 cm⁻¹. $v_{\rm CO}$ for free benzaldehyde occurs at 1698 cm⁻¹. Due to coordination of benzaldehyde to the metal, the stretching frequency of v_{CO} goes down and one of the bands around 1600 cm⁻¹ could be due to v_{co} of benzaldehyde coordinated to ruthenium. Other IR bands are present in free benzaldehyde too but with a slight shift in the position. A strong band at 330 cm^{-1} was observed for $[Ru(AsPh_3)(C_6H_5CHO)_2Cl_2]$. Triphenylarsine also shows absorption around 330 cm^{-1} . Hence this band cannot be assigned unambiguously; however, it may be due to the



Fig. 1. Electronic spectra of (a) $[RuCl_2(PPh_3) (C_6H_5CHO)_2]$ and (b) $[RuCl_2(AsPh_3)(C_6H_5CHO)_2]$ in chloroform.

coupled vibrations of v_{Ru-Cl} and the characteristic vibrations of triphenylarsine.²⁰ The complexes discussed above are diamagnetic, thereby confirming the presence of bivalent ruthenium. These complexes are probably pentacoordinated as suggested by the electronic absorption spectra in chloroform. These spectra (Fig. 1) show one absorption band in the region 760-810 nm and another around 410 nm. The band around 800 nm is observed in ruthenium(II) pentacoordinated squarepyramidal complexes, viz. [RuCl₂(PPh₃)₃] and [RuCl₂(AsPh₃)₂]₂.²⁰ Electronic absorption in this region is generally not observed for octahedrally coordinated complexes of ruthenium(II). Hence, the benzaldehyde complexes seem to have a distorted square-pyramidal structure. The diamagnetic behaviour thus suggests that the six electrons in ruthenium(II) are probably distributed as $(d_{xz}, d_{yz})^4$, d_{xy}^{2} The band around 800 nm could be assigned to $d_{xy} \rightarrow d_{z^2}$ and around 400 nm to $(d_{xz}, d_{yz}) \rightarrow d_{z^2}$ transitions. The complexes are non-conducting in nitrobenzene, thereby confirming non-ionic type of structure for the complexes.

(b) $[Ru(MPh_3)(CO)Cl_2]$

The reaction of ruthenium trichloride, benzaldehyde and triphenylphosphine in *n*-butanol for a period of about 6-8 h yielded a reddish-brown crystalline compound of the composition $[Ru(PPh_3)_2(CO)Cl_2]$. It is diamagnetic in nature and shows a strong and sharp IR absorption at 1980 cm⁻¹ assignable to v_{CO} (terminal). A compound with the same molecular formula and yellow in colour was reported by James *et al.*¹⁹ which showed IR absorptions at 1931 and 1921 cm⁻¹ in Nujol and at 1940 cm⁻¹ in methylene chloride solution for v_{CO} (terminal). It was characterised as a pentacoordinated complex, which apparently isomerized in methylene chloride solution showing a broad band at 1970 cm⁻¹. The reddish-brown compound may be an isomer of the yellow compound reported by James *et al.*¹⁹

Prolonged reaction (~ 20 h) of ruthenium trichloride, benzaldehyde and triphenylphosphine or triphenylarsine resulted in the formation of yellow compounds of the composition $[Ru(CO)(MPh_3)_2Cl_2]$ (M = P or As). These compounds could also be obtained by the reaction of $[RuCl_2(PPh_3)_3]$, $[RuCl_2(PPh_3)_2]_n$ or $[RuCl_2(AsPh_3)_2]_2$ with benzaldehyde in *n*-butanol or by the reaction of $[RuCl_2(MPh_3)(C_6H_5CHO)_2]$ with the corresponding triphenylphosphine or arsine in *n*-butanol. Formation of these carbonyl containing complexes is due to the extraction of a carbonyl group from a benzaldehyde molecule, either coordinated to the metal or free (present in the reaction medium). The infrared spectra of these yellow carbonyl complexes show a strong and sharp band at 1940 cm⁻¹ assignable to v_{CO} (terminal), and all other bands due to triphenylphosphine or triphenylarsine. Yellow [Ru(CO)(PPh₃)₂Cl₂] obtained by us may be same as reported by James et al.19

(c) Reactions of $[Ru(MPh_3)(C_6H_5CHO)_2Cl_2]$ (M = P or As) with donor solvents

Reactions of $[Ru(MPh_3)(C_6H_5CHO)_2Cl_2]$ (M = P or As) with donor solvents were carried out to find out the ease of substitution of the coordinated benzaldehyde. The donor solvents used were pyridine, N,N-dimethylformamide (DMF), and dimethylsulphoxide (DMSO).

Reactions with pyridine or DMF results in the formation of the six coordinate species $[Ru(MPh_3)L_3Cl_2]$ (L = py or DMF) because two molecules of benzaldehyde in the original complexes are replaced by three molecules of pyridine or DMF. The inability to form hexacoordinate complexes with benzaldehyde may be due to partial blocking of the sixth coordination site by the phenyl groups of the two benzaldehyde molecules or the triphenylarsine or phosphine molecule. The IR spectra of the complexes containing DMF showed a very strong band at 1640 cm⁻¹ which is due to v_{co} of DMF coordinate through the oxygen atom.²² In the case of pyridine complexes, all bands due to coordinated pyridine were observed besides bands due to triphenylphosphine or triphenylarsine in the IR region. A medium-sharp band at 1445 cm⁻¹ characteristic of pyridine was also observed.

Pyridine or DMF containing complexes are

diamagnetic, thereby confirming that ruthenium(II) is present in the low-spin state. The electronic absorption spectra of these complexes showed two bands one in the region 450-550 nm and other one in the region 415-390 nm, with a molar extinction coefficient of the order of 10^2-10^3 . These bands may be assigned to ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ transitions respectively. The values of the molar extinction coefficient (~ 10³) are relatively high but this may be due to the mixing of the energy levels with the charge-transfer band(s) in that region.²² These complexes are non-electrolytes in nitrobenzene, thereby confirming their non-ionic character.

Reaction of DMSO with

$$[Ru(MPh_3)(C_6H_5CHO)_2Cl_2]$$

resulted in the substitution of all the benzaldehyde and triphenylphosphine or triphenylarsine molecules by DMSO and gave [Ru(Cl₂(DMSO)₄]. The DMSO complex showed strong IR absorptions at 1120, 1090 and 915 cm⁻¹. The former two absorptions could be due to $v_{S=O}$ of the S-bonded DMSO and the later one due to $v_{S=O}$ of the Obonded DMSO. The complex was same as reported by Evans *et al.*²⁷

(d) Reactions of $[Ru(CO)(MPh_3)_2Cl_2](M = P \text{ or } As)$ with pyridine

Reddish-brown or yellow compounds of the composition $[Ru(CO)(MPh_3)_2Cl_2]$ (M = P or As), on treatment with pyridine resulted in the formation of $[Ru(CO)(MPh_3)(py)_2Cl_2]$, which showed all IR absorptions due to triphenylphosphine or triphenyl-arsine and pyridine. A band at 1444 cm⁻¹ characteristic of pyridine was observed. Besides, two or three bands in the region 1965–1920 cm⁻¹ due to v_{CO} were also observed.

The potential of some of the above mentioned pentacoordinated complexes to act as homogenous catalysts is being examined.

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