Pergamon

Polyhedron Vol. 15, No. 14, pp. 2433–2437, 1996

0277–5387/96 $15.00 + 0.00

0277–5387(95)00506–4

SYNTHESIS OF SOME NOVEL COMPLEXES OF RUTHENIUM(II) CONTAINING AROMATIC ALDEHYDE AND OTHER MONODENTATE LIGANDS AND SOME OF THEM CATALYSED FOR AEROBIC OXIDATION OF TRIPHENYLPHOSPHINE

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(*Received* 26 *July* 1995, *accepted* 2 *October* 1995)

Abstract—The synthesis and characterization of some penta-coordinated ruthenium(II) complexes, *viz*. $[RuX_2(MPh_3)L_2]$ (X = Cl or Br; M = P or As; L = *o*-HOC_6H_4CHO or *p*-$CH_3OC_6H_4CHO$) have been described. The compounds were characterized by physicochemical and spectroscopic methods. The catalytic oxidation of PPh_3 in the presence of molecular oxygen by $[RuBr_2(PPh_3)L_2]$ (L = *o*-HOC_6H_4CHO or *p*-$CH_3OC_6H_4CHO$) has also been studied. Copyright © 1996 Elsevier Science Ltd.

The chemistry of the complexes of ruthenium(II) and ruthenium(III) containing weak donor ligands such as dimethylsulfoxide, acetonitrile, pyridine, benzaldehyde and other aromatic aldehydes is lacking in comparison to the chemistry involving other donor ligands[1–9]. Complexes of ruthenium(II) containing weak donor ligands have a strong potential to act as catalysts in various homogeneous reactions.[1]

Most of the complexes of ruthenium(II) and ruthenium(III) of the type discussed above involve six-coordination around the metal ion. Penta-coordinated complexes have a strong potential to act as catalysts in various homogeneous reactions.[10] The catalytic oxidation of organic substrates is of importance in synthetic organic chemistry both in large-scale processes and in the manufacturing of fine chemicals.[11–14] In view of that, we synthesized some penta-coordinated complexes of ruthenium(II) containing weak donor ligands, *viz*. salicylaldehyde or anisaldehyde and explored the catalytic activity of some of these complexes towards the oxidation of triphenylphosphine to triphenylphosphineoxide by molecular oxygen.

EXPERIMENTAL

All the chemicals used were reagent grade. Ruthenium trichloride trihydrate was obtained from Arora Mathey Ltd, Calcutta. The analyses for the chlorides and bromides were carried out by standard methods after decomposition with a KOH and KNO_3 mixture.[15] Carbon and hydrogen analyses were obtained from RSIC-CDRI, Lucknow. The analytical data are presented in Table 1. IR spectra were recorded using KBr pellets on a Perkin–Elmer 1600 series FTIR spectrophotometer in the range 4000–500 cm^{-1} and a Perkin–Elmer 983 spectrophotometer in the range 4000–180 cm^{-1}. ^1H NMR spectra were recorded on a Varian EM-390 90 MHz spectrometer in $CDCl_3$. Electronic absorption spectra were recorded in solution on a Hitachi U-3210 spectrophotometer in the 1000–250 nm range. The results are given in Table 2. Conductivity measurements were made on a Systronic conductivity meter 304 with millimolar solutions in MeCN. All the melting points are uncorrected.

Preparations

$[RuCl_2(MPh_3)(HOC_6H_4CHO)_2]$ (M = P *or* As). To a solution of ruthenium trichloride trihydrate (0.2 g) in ethanol (10 cm^3) was added salicyl-

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Table 1. Physical and analytical data of new ruthenium(II) compounds

Compound	Colour	Melting point (°C)	Found (Calc.) (%) C	H	X[a]
$[RuCl_2(PPh_3)(HOC_6H_4CHO)_2]$	Brown	172	56.9 (56.6)	4.4 (4.0)	10.2 (10.5)
$[RuCl_2(AsPh_3)(HOC_6H_4CHO)_2]$	Green	220	53.8 (53.2)	4.0 (3.7)	10.4 (9.8)
$[RuCl_2(PPh_3)(CH_3OC_6H_4CHO)_2]$	Brown	142	57.8 (57.8)	4.3 (4.4)	10.1 (10.0)
$[RuCl_2(AsPh_3)(CH_3OC_6H_4CHO)_2]$	Brown	212	54.2 (54.4)	4.1 (4.1)	10.0 (9.5)
$[RuBr_2(PPh_3)(HOC_6H_4CHO)_2]$	Reddish-brown	165	49.8 (50.1)	3.2 (3.5)	20.9 (20.9)
$[RuBr_2(AsPh_3)(HOC_6H_4CHO)_2]$	Dark-violet	190	47.2 (47.3)	3.1 (3.3)	19.5 (19.7)
$[RuBr_2(PPh_3)(CH_3OC_6H_4CHO)_2]$	Reddish-brown	140	50.9 (51.3)	3.5 (3.9)	22.6 (22.6)
$[RuBr_2(AsPh_3)(CH_3OC_6H_4CHO)_2]$	Reddish-brown	168	49.0 (48.6)	3.9 (3.7)	18.6 (19.1)

[a] X = Cl or Br.

aldehyde (1 cm^3) and the mixture was refluxed for 1 h. A solution of triphenylphosphine (0.5 g) or triphenylarsine (0.6 g). in ethanol (5 cm^3) was then added to the hot solution. The resulting solution was refluxed for about 30 min or 1 h in the case of triphenylphosphine or triphenylarsine respectively, when a brown compound in the case of triphenylphosphine and green in the case of triphenylarsine separated out. The compound was centrifuged and washed first with ethanol and then

Table 2. ^1H NMR and electronic absorption spectral data of the ruthenium(II) complexes

Compound	δ (ppm)[a]	λ_{max} (nm)	(ε)
$[RuCl_2(PPh_3)(HOC_6H_4CHO)_2]$	10.12, 7.88, 7.66, 7.31	636	(340)
		505 (sh)	
		405	(1932)
		355	(2525)
$[RuCl_2(AsPh_3)(HOC_6H_4CHO)_2]$	10.10, 8.12, 7.50, 7.36	620	(350)
		400	(2713)
		315	(8310)
		260	(14,146)
$[RuCl_2(PPh_3)(CH_3OC_6H_4CHO)_2]$	10.00, 7.70, 7.30, 7.36, 3.94	678	(413)
		410 (sh)	
		350	(2313)
$[RuCl_2(AsPh_3)(CH_3OC_6H_4CHO)_2]$	10.14, 7.60, 7.35, 3.81	850	(751)
		420	(3381)
		354	(3847)
$[RuBr_2(PPh_3)(HOC_6H_4CHO)_2]$	10.12, 7.89, 7.66, 7.39	862	(653)
		478	(1784)
$[RuBr_2(AsPh_3)(HOC_6H_4CHO)_2)_2]$	9.90, 8.10, 7.58, 7.35	646	(890)
		510	(1250)
		435 (sh)	
$[RuBr_2(PPh_3)(CH_3OC_6H_4CHO)_2]$	10.12, 7.72, 7.70, 7.41, 3.80	862	(795)
		462	(2292)
$[RuBr_2(AsPh_3)(CH_3OC_6H_4CHO)_2]$	10.12, 7.75, 7.40, 3.90	608	(345)
		422 (sh)	

[a] NMR in $CDCl_3$; sh: shoulder.

with diethylether and dried *in vacuo*. The compounds were analysed for $[RuCl_2(MPh_3)(HOC_6H_4CHO)_2]$ (M = P or As); yield: 70–75%.

$[RuCl_2(MPh_3)(CH_3OC_6H_4CHO)_2]$ (M = P *or* As). A reaction similar to $[RuCl_2(MPh_3)(HOC_6H_4CHO)_2]$ was performed using anisaldehyde (1 cm^3) instead of salicylaldehyde and the refluxing time for the final mixture was 1 or 2 h for triphenylphosphine or triphenylarsine, respectively. A brown compound was isolated as in the preparation of $[RuCl_2(MPh_3)(HOC_6H_4CHO)_2]$. It was analysed for $[RuCl_2(MPh_3)(CH_3OC_6H_4CHO)_2]$ (M = P or As); yield: 60–65%.

$[RuBr_2(MPh_3)(CH_3OC_6H_4CHO)_2]$ (M = P *or* As). To a solution of ruthenium trichloride trihydrate (0.1 g) in ethanol (10 cm^3) LiBr (0.4 g) was added and the mixture was refluxed for 30 min. Anisaldehyde (1 cm^3) was added to the mixture, refluxed for a further 15 min and a solution of triphenylphosphine (0.2 g) or triphenylarsine (0.3 g) in ethanol (10 cm^3) was added. The resulting solution was refluxed for a further period of 1 h, when a reddish-brown compound separated out. It was centrifuged, washed first with ethanol and then with diethylether and dried *in vacuo*. It was analysed for $[RuBr_2(MPh_3)(CH_3OC_6H_4CHO)_2]$ (M = P or As); yield: 75–80%.

$[RuBr_2(MPh_3)(HOC_6H_4CHO)_2]$ (M = P *or* As). A reaction similar to that of $[RuBr_2(MPh_3)(CH_3OC_6H_4CHO)_2]$ was performed using salicylaldehyde instead of anisaldehyde. A reddish-brown compound was isolated as in the preparation of $[RuBr_2(MPh_3)(CH_3OC_6H_4CHO)_2]$. It was analysed for $[RuBr_2(MPh_3)(HOC_6H_4CHO)_2]$ (M = P or As); yield: 70–75%.

Catalytic oxidation of triphenylphosphine

$[RuBr_2(PPh_3)L_2]$ (L = HOC_6H_4CHO or $CH_3OC_6H_4CHO$) has been used in the presence of molecular oxygen, for catalytic oxidation of PPh_3 to $OPPh_3$. A typical reaction using $[RuBr_2(PPh_3)(HOC_6H_4CHO)_2]$ as the catalyst and PPh_3 (molar ratio 1 : 20) is described below.

A solution of $[RuBr_2(PPh_3)(HOC_6H_4CHO)_2]$ (0.2 g) in n-butanol (10 cm^3) was added to a solution of triphenylphosphine (1.36 g) in n-butanol (10 cm^3) and the mixture was refluxed to boiling on an oil bath for 5 h, while oxygen was slowly bubbled through the solution. The solution was cooled to room temperature and a compound was separated by centrifugation. The solvent was removed from the mother liquor under reduced pressure and a white mass was obtained. It was washed several times with diethylether to free it from PPh_3 and dried *in vacuo*. It was analysed for $OPPh_3$; m.p. 154–156°C; yield: 1.04 g, 72%.

RESULTS AND DISCUSSION

Elemental analyses indicate that the complexes have the formula $[RuX_2(MPh_3)L_2]$ (X = Cl or Br; M = P or As; L = HOC_6H_4CHO or $CH_3OC_6H_4CHO$). All the complexes are diamagnetic at room temperature, confirming a low spin d^6 configuration of ruthenium(II) and they are non-electrolytes in MeCN.

The ^1H NMR spectra of the complexes showed a similar pattern (Table 2). In the spectra the aldehyde proton singlet appeared in the region δ10.14–9.90 and the methoxy group of *p*-anisaldehyde was observed in the 3.94–3.80 δ range.[16] Further, the multiple peaks of substituted aromatic protons resonate in the 8.12–7.31 δ range due to triphenylphosphine or triphenylarsine and salicylaldehyde or anisaldehyde. The ratio of the area under the signals at different regions suggests the appropriate composition of the complex.

The IR spectra of the complexes showed all the characteristic bands due to triphenylphosphine or triphenylarsine and coordinated L. In the case of the salicylaldehyde-containing complex two bands of medium intensity appear in the region 1609–1577 cm^{-1}, strongly indicative of the coordination of the carbonyl oxygen of the aldehyde to the metal, otherwise $\nu_{(CO)}$ for free salicylaldehyde is expected at 1660 cm^{-1}. A strong band at 1600 cm^{-1} in the anisaldehyde ligand spectra is characteristic of $\nu_{(CO)}$. In the metal complexes of the anisaldehyde ligand this band is shifted to a lower frequency in the region 1589–1556 cm^{-1}, which indirectly supports carbonyl oxygen bonding to the metal ion. The low frequency band appearing in the region 521–475 cm^{-1} is tentatively assigned to the $\nu_{(Ru-O)}$ vibration. The presence of a medium band in the far-IR region 326–323 cm^{-1} in the case of $[RuCl_2(MPh_3)L_2]$ is characteristic of $\nu_{(Ru-Cl)}$ of the complex.

Electronic spectra

The electronic absorption spectra of most of the complexes in chloroform show three types of bands (Table 2). The intense absorption in the vis region is typical of *d–d* transition bands, similar to those observed in the analogous penta-coordinated square-pyramidal ruthenium(II) compounds.[7,17] Hence, these complexes seem to have a distorted square-pyramidal structure. Assuming an axial distortion, from the octahedral geometry, the first band in the region 862–500 nm and second absorp-

Table 3. Oxidation of triphenylphosphine with ruthenium(II) compounds

Catalyst	Molar ratio Catalyst : PPh_3	Quantity (g) Catalyst	PPh_3	$OPPh_3$	Yield (%)
$[RuBr_2(PPh_3)(HOC_6H_4CHO)_2]$	1 : 5	0.2	0.34	0.28	78
$[RuBr_2(PPh_3)(HOC_6H_4CHO)_2]$	1 : 10	0.2	0.68	0.54	75
$[RuBr_2(PPh_3)(HOC_6H_4CHO)_2]$	1 : 15	0.2	1.02	0.83	77
$[RuBr_2(PPh_3)(HOC_6H_4CHO)_2]$	1 : 20	0.2	1.36	1.04	72
$[RuBr_2(PPh_3)(CH_3OC_6H_4CHO)_2]$	1 : 5	0.2	0.33	0.27	77
$[RuBr_2(PPh_3)(CH_3OC_6H_4CHO)_2]$	1 : 10	0.2	0.66	0.52	74
$[RuBr_2(PPh_3)(CH_3OC_6H_4CHO)_2]$	1 : 20	0.2	1.32	0.98	70
No catalyst		0.0	2.00	0.00	

tion bands in the region 500–400 nm could be assigned to $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1A_2$ transitions, respectively.[18] The ε value for the second absorption band is of the order 10^3, which is higher than the *d–d* transition in second-row transition metals. Hence, this band may have a contribution from the charge-transfer transition ruthenium(II) → ligand, besides involving $^1A_1 \rightarrow {}^1A_2$. The third band in the region 355–260 nm has an ε value of the order of 10^4, which suggests it to be either a charge-transfer band or an allowed transition as observed in the ligand. The absorption at 260 nm in the case of $[RuCl_2(AsPh_3)(HOC_6H_4CHO)_2]$ may be assigned to the $\pi \rightarrow \pi^*$ transition of the carbonyl group of the salicylaldehyde molecules[19] and the absorption band in the region 355–315 nm in the case of $[RuCl_2(MPh_3)L_2]$ ($M = P$ or As; $L = HOC_6H_4CHO$ or $CH_3OC_6H_4CHO$) could be assigned to a combination of $\pi \rightarrow \pi^*$ of the aldehyde and the ruthenium(II) → Cl charge-transfer transition.

Catalytic activity of $[RuBr_2(PPh_3)L_2]$ ($L = HOC_6H_4CHO$ *or* $CH_3OC_6H_4CHO$)

$[RuBr_2(PPh_3)L_2]$ ($L = C_4H_3OCHO$ or C_6H_5CHO) has been used in the presence of molecular oxygen for the catalytic oxidation of triphenylphosphine to triphenylphosphineoxide.[9] Similarly, $[RuBr_2(PPh_3)L_2]$ ($L = HOC_6H_4CHO$ or $CH_3OC_6H_4CHO$) was used to oxidize PPh_3 to $OPPh_3$ in the presence of molecular oxygen. The reactions were carried out by taking different molar ratios of catalyst : PPh_3 (1 : 5–1 : 20) and in all cases 70–80% of $OPPh_3$ was obtained. The results are given in Table 3. There is no oxidation of PPh_3 by molecular oxygen in the absence of the catalyst. The $OPPh_3$ was characterized by carbon and hydrogen analyses, melting point determination and IR spectroscopy. The IR spectrum of $OPPh_3$ showed a strong sharp band at 1185 cm^{-1}, characteristic of $\nu_{(P=O)}$.[8] The mechanism of oxidation of PPh_3 by molecular oxygen using $[RuBr_2(PPh_3)L_2]$ ($L = HOC_6H_4CHO$ or $CH_3OC_6H_4CHO$) may be similar to $[RuBr_2(PPh_3)L_2]$ ($L = C_4H_3OCHO$ or C_6H_5CHO) as reported earlier.[9]

Acknowledgements—One of the authors (B.C.P.) is thankful to Gauhati University for the award of the Thaneswar Baruah Post-doctoral fellowship in Chemistry. The authors thank RSIC-CDRI, Lucknow, for the micro-analytical data and RSIC-NEHU, Shillong, for recording the IR and ^1H NMR spectra.

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