Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganic Chemistry Communications 6 (2003) 486–490

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

Synthesis, characterization and catalytic activities of ruthenium complexes containing triphenylphosphine/triphenylarsine and tetradentate Schiff bases ☆

R. Karvembu, S. Hemalatha, R. Prabhakaran, K. Natarajan *

Department of Chemistry, Bharathiar University, Coimbatore 641 046, India

Received 24 October 2002; accepted 3 January 2003

Abstract

Ruthenium(II) complexes of the type [Ru(CO)(B)(L)] (B = $AsPh_3$, pyridine, piperidine or morpholine; L = dianion of tetradentate Schiff bases) have been synthesized and characterized by physico-chemical methods. These complexes are found to be effective catalysts in the oxidation of primary and secondary alcohols using *N*-methylmorpholine-*N*-oxide as oxidant. The catalytic activity of these triphenylarsine complexes have been compared with that of triphenylphosphine complexes and with similar ruthenium(III) complexes. The formation of high valent $Ru^{n+2}{=}O$ species as catalytic intermediate is proposed for the catalytic processes.

Keywords: Ruthenium(II) triphenylarsine complexes; Tetradentate Schiff bases; Catalytic oxidation study; Intermediate ruthenium-oxo species

1. Introduction

Catalytic oxidation of alcohols is an important industrial process due to the wide variety of products synthesized by this route. Three important natural enzymes used for oxidation reactions are cytochrome P-450, peroxidases and catalases. All these enzymes have iron(III) porphyrin as the central unit. Hence, several investigations have been made on the reactions of synthetic metalloporphyrins to understand the mechanism of action of porphyrin containing enzymes [1]. Though metalloporphyrins catalyse oxidation reactions, the catalytic yield is not satisfactory to have any commercial viability. Moreover, it is not easy to synthesize metalloporphyrins and this led scientists to look for other ligands to make novel complexes to be employed as catalysts in oxidation reactions [2–7]. Hence, studies on synthesis and catalytic activity of metal complexes derived from "salen" type ligands have gained greater momentum [8]. Besides, the catalytic activity of ruthenium complexes with tertiary phosphine or tertiary arsine ligand is well documented [9].

We have previously reported the catalytic oxidation properties of several ruthenium complexes containing tertiary phosphine or tertiary arsine and β-diketones [10,11]. In the present work, we report the synthesis, spectral characterization and catalytic activity of some ruthenium(III) tetradentate Schiff base complexes with triphenylarsine. We have also compared the catalytic oxidation properties of several ruthenium(II) and ruthenium(III) complexes which have similar structure. The general structure of the Schiff base ligands used in this study is given in Fig. 1.

2. Experimental

2.1. Materials

The compound $[RuHCl(CO)(AsPh_3)_3]$, and Schiff base ligands were prepared according to literature methods [12,13]. The complexes of the type

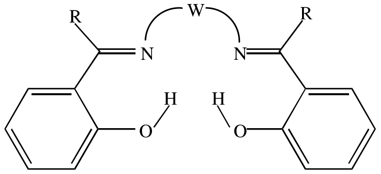
---

☆ Presented in the 35th International Conference on Coordination Chemistry, 21–26 July, 2002; University of Heidelberg, Germany.

* Corresponding author. Tel.: +91-422-242-2222; fax: +91-422-242-2387.

E-mail address: k_natraj6@yahoo.com (K. Natarajan).

1387-7003/03/$ - see front matter © 2003 Published by Elsevier Science B.V.
doi:10.1016/S1387-7003(03)00021-2



R	W	Abbreviation
H	C_6H_4	H_2L^1
H	$(CH_2)_4$	H_2L^2
CH_3	$(CH_2)_4$	H_2L^3

Fig. 1. Structure of Schiff base ligands.

$[RuHCl(CO)(AsPh_3)_2(B)]$, (B = pyridine, piperidine, morpholine) have been prepared by the modified procedure [14]. Instrumental details for elemental analysis, IR, UV–Vis and NMR spectra are the same as described earlier [10].

2.2. Synthesis of complexes of the type [Ru(CO)(B)(L)] (B = AsPh₃, py, pip or mor; L = dianion of tetradentate Schiff base)

To a solution of $[RuHCl(CO)(AsPh_3)_2(B)]$ (B = $AsPh_3$, py, pip or mor) (0.1 g, 0.092–0.117 mmol) in benzene (25 cm^3), the Schiff base (0.027–0.038 g, 0.092–0.117 mmol) was added and the mixture was heated under reflux for 6 h. The resulting solution was concentrated to ca. 3 cm^3 and cooled. A small quantity of petroleum ether (60–80 °C) was added to the concentrated solution and the precipitated complex was filtered off, washed with petroleum ether and recrystallized from CH_2Cl_2/petroleum ether (60–80 °C) mixture and dried in vacuo.

2.3. Oxidation of benzyl alcohol and cyclohexanol

To a solution of alcohol (1 mmol) in dichloromethane (20 cm^3) was added, *N*-methylmorpholine-*N*-oxide (NMO) (3 mmol) and the ruthenium complex (0.01 mmol). The solution was stirred for 3 h at room temperature, then the mixture was evaporated to dryness and extracted with petroleum ether (60–80 °C) (2 × 25 cm^3). The combined petroleum ether extracts were evaporated to give corresponding aldehyde which was then quantified as 2,4-dinitrophenylhydrazone derivative [15].

3. Results and discussion

The tetradentate Schiff bases (H_2L) on reacting with ruthenium(II) complexes, $[RuHCl(CO)(AsPh_3)_2(B)]$ yielded new complexes of the type [Ru(CO)(B)(L)] (where B = pyridine (py), piperidine (pip) or morpholine (mor); L = dianionic tetradentate Schiff base).

$$[RuHCl(CO)(AsPh_3)_2(B)] + H_2L \rightarrow [Ru(CO)(B)(L)] + 2AsPh_3 + H_2 + HCl$$

The analytical data obtained for the compounds do confirm the molecular formula suggested for the new complexes. The analytical data and the spectral data of the complexes are given in Tables 1–3, respectively. In all the reactions, the Schiff bases replace two triphenylarsines, a chloride and a hydride from the starting complexes leading to the new hexa coordinated complexes. The Schiff bases in all these complexes behave as dibasic tetradentate ligands. One interesting aspect is that in all the new complexes, the heterocyclic nitrogen bases (pyridine, piperidine or morpholine) remain intact without being replaced. The reason for non-replacement of the coordinated bases is due to the fact that the Ru–As bond is more labile compared to Ru–N bond because of better σ donating ability of nitrogen [14]. The same observation has been made for triphenylphosphine complexes of ruthenium [11].

The free Schiff bases show a very strong absorption around 1620–1600 cm^{-1} in their IR spectra which is characteristic of the azomethine (C=N) group. In the IR spectra of the new complexes, the absorption due to C=N is observed at a lower region (1610–1580 cm^{-1}), indicating the coordination of nitrogen atom of the Schiff base to ruthenium [16]. A strong band observed around

Table 1
Analytical data of data of ruthenium(II) Schiff base complexes

Complexes	Molecular formula	Color	Yield (%)	M.p (°C)	Elemental analyses found (Calc.) (%)		
					Carbon	Hydrogen	Nitrogen
$[Ru(CO)(AsPh_3)(L^1)]$	$C_{39}H_{29}N_2O_3AsRu$	Reddish orange	67	144	62.01 (62.4)	3.67 (3.89)	3.50 (3.74)
$[Ru(CO)(py)(L^1)]$	$C_{26}H_{19}N_3O_3Ru$	Brown	60	69	59.81 (59.77)	3.37 (3.67)	7.81 (8.04)
$[Ru(CO)(pip)(L^1)]$	$C_{26}H_{25}N_3O_3Ru$	Reddish brown	58	78	58.71 (59.08)	4.87 (4.77)	7.59 (7.95)
$[Ru(CO)(mor)(L^1)]$	$C_{26}H_{23}N_3O_4Ru$	Brick red	64	80	56.39 (56.60)	4.02 (4.37)	7.59 (7.92)
$[Ru(CO)(AsPh_3)(L^2)]$	$C_{37}H_{33}N_2O_3AsRu$	Yellowish brown	69	127	60.57 (60.91)	4.22 (4.56)	3.54 (3.84)
$[Ru(CO)(py)(L^2)]$	$C_{24}H_{23}N_3O_3Ru$	Yellow	60	109	57.08 (57.36)	4.27 (4.61)	7.97 (8.36)
$[Ru(CO)(pip)(L^2)]$	$C_{24}H_{29}N_3O_3Ru$	Yellowish green	62	84	56.41 (56.68)	5.41 (5.75)	8.39 (8.26)
$[Ru(CO)(mor)(L^2)]$	$C_{23}H_{27}N_3O_4Ru$	Pale brown	61	87	53.89 (54.11)	5.02 (5.33)	7.84 (8.23)
$[Ru(CO)(AsPh_3)(L^3)]$	$C_{39}H_{37}N_2O_3AsRu$	Yellowish brown	72	115	61.50 (61.82)	4.52 (4.92)	3.50 (3.70)
$[Ru(CO)(AsPh_3)(L^3)]$	$C_{26}H_{27}N_3O_3Ru$	Yellowish green	58	99	58.56 (58.86)	5.02 (5.13)	7.60 (7.92)
$[Ru(CO)(AsPh_3)(L^3)]$	$C_{26}H_{33}N_3O_3Ru$	Brown	62	95	57.89 (58.19)	6.02 (6.20)	7.54 (7.83)
$[Ru(CO)(AsPh_3)(L^3)]$	$C_{25}H_{31}N_3O_4Ru$	Yellowish green	66	98	55.38 (55.75)	5.42 (5.80)	7.45 (7.80)

Table 2
IR and electronic spectral data of ruthenium(II) Schiff base complexes

Compound	Molecular formula	$v_{\mathrm{C=N}}$	$v_{\mathrm{C–O}}$	$v_{\mathrm{C\equiv O}}$	Bands for coordinated nitrogen bases	$\lambda_{\max}$
$[\mathrm{Ru(CO)(AsPh_3)(L^1)}]$	$C_{39}H_{29}N_2O_3AsRu$	1580	1310	1940	–	236,261,330
$[\mathrm{Ru(CO)(py)(L^1)}]$	$C_{26}H_{19}N_3O_3Ru$	1600	1310	1950	1070	232,250,340
$[\mathrm{Ru(CO)(pip)(L^1)}]$	$C_{26}H_{25}N_3O_3Ru$	1605	1320	1930	1088	232,261,333
$[\mathrm{Ru(CO)(mor)(L^1)}]$	$C_{26}H_{23}N_3O_4Ru$	1605	1310	1930	1080	232,373
$[\mathrm{Ru(CO)(AsPh_3)(L^2)}]$	$C_{37}H_{33}N_2O_3AsRu$	1590	1300	1950	–	232,261,344
$[\mathrm{Ru(CO)(py)(L^2)}]$	$C_{24}H_{23}N_3O_3Ru$	1605	1310	1955	1070	232,247,348
$[\mathrm{Ru(CO)(pip)(L^2)}]$	$C_{24}H_{29}N_3O_3Ru$	1600	1320	1927	1070	232,340
$[\mathrm{Ru(CO)(mor)(L^2)}]$	$C_{23}H_{27}N_3O_4Ru$	1600	1320	1932	1090	236,337
$[\mathrm{Ru(CO)(AsPh_3)(L^3)}]$	$C_{39}H_{37}N_2O_3AsRu$	1597	1300	1942	–	232,254,348
$[\mathrm{Ru(CO)(py)(L^3)}]$	$C_{26}H_{27}N_3O_3Ru$	1590	1310	1947	1060	232,243,340
$[\mathrm{Ru(CO)(pip)(L^3)}]$	$C_{26}H_{33}N_3O_3Ru$	1610	1310	1922	1080	236,337
$[\mathrm{Ru(CO)(mor)(L^3)}]$	$C_{25}H_{31}N_3O_4Ru$	1597	1310	1924	1090	236,337

Note. v in $\mathrm{cm^{-1}}$; $\lambda_{\max}$ in nm.

Table 3
^{1}H NMR data of ruthenium(II) complexes

Complexes	^{1}H NMR (ppm)
$[\mathrm{Ru(CO)(AsPh_3)(L^1)}]$	7.02–7.85 [m, aromatic] 8.82 [s, CH]
$[\mathrm{Ru(CO)(mor)(L^1)}]$	3.32 [s, CH_2(1)] 3.95 [s, CH_2(2)] 7.25–7.77 [m, aromatic] 8.64 [s, CH] 8.87 [s, NH]
$[\mathrm{Ru(CO)(pip)(L^2)}]$	3.15 [s, CH_2] 7.26–7.78 [m, aromatic] 8.71 [s, CH] 9.12 [s, NH]

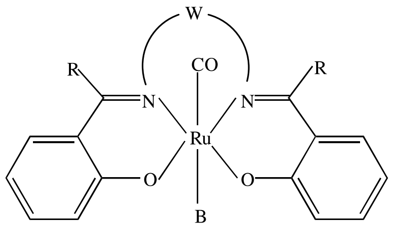
Note. δ in ppm.

1280–1270 $\mathrm{cm^{-1}}$ in the free Schiff bases has been assigned to phenolic C–O stretching. On complexation, this band has been shifted to higher frequency (1320–1300 $\mathrm{cm^{-1}}$) showing the other coordination is through phenolic oxygen atom [17]. This is further supported by the disappearance of the broad band at 2980–2900 $\mathrm{cm^{-1}}$ due to O–H in the complexes. For all the new complexes, the IR spectra showed a strong band in the region 1955–1920 $\mathrm{cm^{-1}}$ due to terminally coordinated carbonyl group. For the complexes, [Ru(CO)(B)(L)] (where B = py, pip or mor; L = dianion of tetradentate Schiff base), the IR spectra showed a medium intensity band in the region 1090–1070 $\mathrm{cm^{-1}}$ which is characteristic of coordinated nitrogen bases [14]. Characteristic bands for triphenylarsine are also present in the expected region.

The electronic spectra of the complexes were recorded in dichloromethane. The electronic spectra of the complexes showed two to three bands in the region 375–230 nm. The bands appearing in the region 375–330 nm have been assigned to the spin allowed transition $^1A_{1g} \rightarrow {}^1T_{1g}$. This assignment is in conformity with the assignments made for similar other octahedral complexes [18]. The other bands around 265–230 nm have been assigned to charge transfer transitions.

^{1}H NMR spectra of the complexes $[\mathrm{Ru(CO)(AsPh_3)(L^1)}]$, $[\mathrm{Ru(CO)(mor)(L^1)}]$ and $[\mathrm{Ru(CO)(pip)(L^2)}]$ have been recorded to confirm the binding of Schiff bases to the ruthenium ion and to find out the presence of triphenylarsine or heterocyclic nitrogen bases. The spectra of all the three complexes showed a singlet in the region 8.64–8.82 ppm which has been assigned to azomethine proton. The spectra of $[\mathrm{Ru(CO)(mor)(L^1)}]$ and $[\mathrm{Ru(CO)(pip)(L^2)}]$ showed a singlet at 8.87 and 9.12 ppm, respectively, which have been assigned due to NH proton of piperidine and morpholine. This signal is not found in $[\mathrm{Ru(CO)(AsPh_3)(L^1)}]$. This confirms the presence of coordinated nitrogen base in these complexes. Further, the signal for methylene protons appears as a broad singlet in the region 3.15–3.95 ppm in $[\mathrm{Ru(CO)(pip)(L^2)}]$. The spectra of $[\mathrm{Ru(CO)(mor)(L^1)}]$ showed two signals for methylene protons, one at 3.23 ppm which is due to methylene protons nearer to oxygen and another signal at 3.95 ppm which is due to methylene protons nearer to nitrogen. The multiplet observed around 7.02–7.85 ppm in all the three complexes have been assigned to the protons of phenyl group of the triphenylarsine and ligands.

On the basis of elemental analyses, IR, electronic and ^{1}H NMR spectral data, the following octahedral structure has been proposed for the new ruthenium(II) complexes.



B = $AsPh_3$, py, pip or mor.
R = H or CH_3
W = C_6H_4, $(CH_2)_4$

3.1. Catalytic activity

The oxidation of benzyl alcohol and cyclohexanol was carried out with new ruthenium(II) complexes in the presence of NMO as oxidant and dichloromethane as solvent. The data of catalytic oxidation is given in Table 4. The catalytic efficiency was compared with the previously reported [16,19] similar triphenylphosphine ruthenium(II) and ruthenium(III) complexes. Benzaldehyde was formed from benzyl alcohol and cyclohexanol was converted into cyclohexanone after stirring for about 3 h, which was then quantified as its 2,4-dinitrophenylhydrazone derivatives. In no case was there any detectable oxidation of alcohols in the presence of NMO alone and without the ruthenium complex.

The relatively higher product yield obtained for oxidation of benzyl alcohol compared to cyclohexanol is due to the fact that α-CH unit of benzyl alcohol is more acidic than cyclohexanol [20]. Complexes that do not contain heterocyclic nitrogen bases exhibit better catalytic activity than the complexes with heterocyclic nitrogen bases. This result is in accord with our observation, taking into account the stronger binding of heterocyclic bases to ruthenium ion, as compared to triphenylarsine. The formation of the active species is therefore less favored in the former case than in the latter, resulting in lower yield [11]. The triphenylphosphine ruthenium(II) complexes possess greater catalytic activity than that of the triphenylarsine complexes. The same observation has been made recently [21].

Ruthenium(II) complexes exhibit better catalytic activity than similar ruthenium(III) complexes, attributed to more lability of Ru(II)–P bond compared to Ru(III)–P bond. Besides, the catalytic efficiency of the complexes derived from *o*-hydroxyacetophenone and diamines is lower than the one derived from salicylaldehyde and diamines. The essential difference between these two complexes is that the hydrogen atom of the aldehyde group of salicylaldehyde is replaced by a methyl group in the 2-hydroxyacetophenone complex. Hence, it seems that the presence of the electron-donating methyl group enhances the catalytic activity of the acetophenone complex over the salicylaldehyde complex. This is in agreement with the earlier observation [22]. However, there is also a report in which the catalytic activity is increased by electron donating substituent [23].

Table 4
Catalytic oxidation data of alcohols by ruthenium(II) Schiff base complexes in the presence of *N*-methylmorpholine-*N*-oxide

Complexes	Substrate	Product	Yield (%)	Turnover
$[Ru(CO)(AsPh_3)(L^1)]$	Benzyl alcohol	A	63.6	66
	Cyclohexanol	K	47.2	47
$[Ru(CO)(py)(L^1)]$	Benzyl alcohol	A	54.5	57
	Cyclohexanol	K	37.8	38
$[Ru(CO)(pip)(L^1)]$	Benzyl alcohol	A	45.3	47
	Cyclohexanol	K	37.8	38
$[Ru(CO)(mor)(L^1)]$	Benzyl alcohol	A	45.3	47
	Cyclohexanol	K	28.3	28
$[Ru(CO)(AsPh_3)(L^2)]$	Benzyl alcohol	A	81.0	85
	Cyclohexanol	K	66.3	66
$[Ru(CO)(py)(L^2)]$	Benzyl alcohol	A	54.5	57
	Cyclohexanol	K	37.8	38
$[Ru(CO)(pip)(L^2)]$	Benzyl alcohol	A	27.0	28
	Cyclohexanol	K	28.3	28
$[Ru(CO)(mor)(L^2)]$	Benzyl alcohol	A	62.7	66
	Cyclohexanol	K	56.7	57
$[Ru(CO)(AsPh_3)(L^3)]$	Benzyl alcohol	A	45.3	47
	Cyclohexanol	K	28.3	28
$[Ru(CO)(py)(L^3)]$	Benzyl alcohol	A	18.3	19
	Cyclohexanol	K	9.40	9
$[Ru(CO)(pip)(L^3)]$	Benzyl alcohol	A	27.0	28
	Cyclohexanol	K	19.0	19
$[Ru(CO)(mor)(L^3)]$	Benzyl alcohol	A	18.3	19
	Cyclohexanol	K	9.40	9
$[Ru(CO)(PPh_3)(L^1)]$	Benzyl alcohol	A	90.7	94
	Cyclohexanol	K	75.1	75
$[Ru(CO)(PPh_3)(L^2)]$	Benzyl alcohol	A	81.0	85
	Cyclohexanol	K	75.1	75
$[Ru(Cl)(PPh_3)(L^1)]$	Benzyl alcohol	A	45.3	47
	Cyclohexanol	K	28.3	28
$[Ru(Cl)(AsPh_3)(L^1)]$	Benzyl alcohol	A	27.0	28
	Cyclohexanol	K	9.40	9

An IR spectral change has been observed by the addition of NMO to a dichloromethane solution of $[Ru(CO)(AsPh_3)(L^3)]$. The appearance of a band at 859 cm^{-1} after addition of NMO is attributed to the formation of high valent $Ru^{n+2}{=}O$ species [24]. Hence, it has been concluded that catalytic oxidation proceeds through metal-oxo intermediate.

References

[1] E.D. Stevens, J. Am. Chem. Soc. 103 (1981) 5087.

[2] M.G. Bhowon, Indian J. Chem. 39A (2000) 1207–1209.

[3] M.G. Bhowon, H. Li Kam Wah, R. Narain, Polyhedron 18 (1998) 341–345.

[4] T. Jeewoth, H. Li Kam Wah, M.G. Bhowon, D. Ghoorohoo, K. Babooram, Synth. React. Inorg. Met-Org. Chem. 30 (6) (2000) 1023–1038.

[5] A.M. El-Hendawy, A. El-Ghany El-Kourashy, M.M. Shanab, Polyhedron 11 (1992) 523.

[6] A.M. El-Hendawy, A.H. Alkubaisi, A. El-Ghany El-Kourashy, M.M. Shanab, Polyhedron 12 (1993) 2343.

[7] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, J. Mol. Cat. 96 (1995) 17.

[8] K. Srinivasan, S. Perrier, J.K. Kochi, J. Mol. Cat. 36 (1986) 297.

[9] W.K. Wong, X.P. Chen, J.P. Guo, Y.G. Chi, W.X. Pan, W.Y. Wong, J. Chem. Soc. Dalton Trans. (2002) 1139.

[10] R. Karvembu, K. Natarajan, Polyhedron 21 (2002) 219.

[11] R. Karvembu, K. Natarajan, Polyhedron 21 (2002) 1721.

[12] R.A. Sanchez-Delgado, W.Y. Lee, S.R. Choi, Y. Cho, M.J. Jun, Trans. Metal Chem. 16 (1991) 241.

[13] P. Pfieffer, T. Hesse, H. Pfitzner, W. Scholl, H. Thielert, J. Prakt. Chem. 149 (1937) 217.

[14] S. Gopinathan, I.R. Unny, S.S. Deshpande, C. Gopinathan, Indian J. Chem. 25A (1986) 1015.

[15] A.I. Vogel, Textbook of Practical Organic Chemistry, fifth ed., Longman, London, 1989.

[16] P. Viswanathamurthi, K. Natarajan, Trans. Metal Chem. 24 (1999) 638.

[17] K. Veno, A.E. Martell, J. Phys. Chem. 60 (1956) 1230.

[18] K. Natarajan, U. Agarwala, Inorg. Nucl. Chem. Lett. 14 (1978) 7.

[19] P. Viswanathamurthi, N. Dharmaraj, S. Anuradha, K. Natarajan, Trans. Metal Chem. 23 (1998) 337.

[20] D. Chatterjeea, A. Mitra, B.C. Roy, J. Mol. Cat. 161 (2000) 17.

[21] J.Y. Kim, M.J. Jun, W.Y. Lee, Polyhedron 15 (1996) 3787.

[22] K. Srinivasan, P. Michand, J.K. Kochi, J. Am. Chem. Soc. 108 (1986) 2309.

[23] P.K. Bhattacharya, Proc. Indian Acad. Sci. (Chem. Sci.) 102 (1990) 247.

[24] C.M. Che, V.W.W. Yan, T.C.W. Mak, J. Am. Chem. Soc. 112 (1990) 2284.