Journal of Organometallic Chemistry, 454 (1993) 237–241

JOM 23488

Paramagnetic organometallics formed by *o*-metallation of phenolic Schiff bases by ruthenium(III)

Prasanta Ghosh, Amitava Pramanik, Nilkamal Bag, Goutam Kumar Lahiri and Animesh Chakravorty

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032 (India)

(Received November 17, 1992)

Abstract

The reaction of $Ru(PPh_3)_3X_2$ (X = Cl, Br) with the Schiff base condensate of 4-substituted benzaldehyde (RC_6H_4CHO) and 2-aminophenol under aerobic conditions affords the complexes $Ru^{III}(RL)(PPh_3)_2X$ in which RL is the Schiff base ligand bound to the metal centre at the phenolic oxygen (deprotonated), azomethine nitrogen and an *ortho* carbon atom (deprotonated) of the benzaldehyde fragment. The complexes behave as one-electron paramagnets; and give rhombic EPR spectra, that have been analysed to furnish values of axial and rhombic distortion parameters as well as the energies of the two expected ligand field transitions within the t_2 shell. One of the transitions has been experimentally observed in the predicted region. The complexes are electroactive and display ruthenium(III)–ruthenium(II) ($E_{1/2}$ −0.5 to −0.8 V *vs.* SCE) and ruthenium(IV)–ruthenium(III) ($E_{1/2}$ 0.4 to 0.8 V) couples. The $E_{1/2}$ values vary linearly with the Hammett constant of the substituent R. The role of phenolato-coordination in stabilizing the trivalent state of ruthenium is noted.

1. Introduction

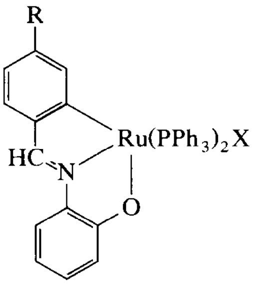
Trivalent ruthenium has a vast coordination chemistry but organometallics incorporating this paramagnetic ion are scarce [1]. Until very recently, a few carbonyl species [2–9] were virtually the only authentic examples of ruthenium(III) organometallics. In the last few years, a small number of noncarbonylic systems having the Ru^{III}–C σ-bond have been characterized, such as azophenolates [10], porphyrinates [11–13] and polypyridyls [14].

We describe below a new family of ruthenium(III) organometallic complexes of tridentate (C,N,O) coordinating Schiff base ligands derived from substituted benzaldehydes and 2-aminophenol. The spectra, magnetism, and electrochemistry of the complexes are reported.

2. Results and discussion

2.1. Synthesis and characterization of the complexes

Ten complexes (general abbreviation Ru(RL)$(PPh_3)_2X$, X = Cl, Br) have been synthesised; **1–5**, **1a–5a**. The Schiff bases were isolated as yellow solids by condensing substituted benzaldehydes with 2-aminophenol in ethanol. When these are treated with $Ru(PPh_3)_3X_2$ (X = Cl, Br) in the mole ratio 1.5:1 in boiling ethanol in air, dark violet solutions are formed from which $Ru(RL)(PPh_3)_2X$ separates as a dark solid. The oxidation of the metal on going from the starting material to the product is brought about by aerial oxygen (see below). The complexes are very soluble in benzene and dichloromethane, affording electrically non-conducting violet solutions. Elemental analysis data are set out in Table 1.



R	X = Cl	X = Br
OMe	**1**	**1a**
Me	**2**	**2a**
H	**3**	**3a**
Cl	**4**	**4a**
NO_2	**5**	**5a**

Correspondence to: Professor A. Chakravorty.

0022-328X/93/$6.00

TABLE 1. Analytical and IR spectral data

Compound	Elemental analysis(%) [a]			IR spectral data	
	C	H	N	ν(RuCl) (cm^{-1})	ν(C=N) [b] (cm^{-1})
1	67.64(67.75)	4.67(4.63)	1.54(1.58)	340	1580(1610)
2	69.11(69.00)	4.69(4.71)	1.59(1.61)	340	1570(1615)
3	68.64(68.72)	4.51(4.56)	1.67(1.64)	330	1575(1620)
4	65.89(66.06)	4.28(4.27)	1.55(1.57)	330	1570(1620)
5	65.32(65.29)	4.29(4.22)	3.10(3.11)	335	1565(1620)
1a	64.63(64.51)	4.49(4.41)	1.47(1.51)	-	1570(1610)
2a	65.77(65.64)	4.47(4.49)	1.57(1.53)	-	1575(1615)
3a	65.47(65.33)	4.23(4.33)	1.62(1.56)	-	1580(1620)
4a	62.61(62.91)	4.02(4.07)	1.51(1.50)	-	1575(1620)
5a	62.31(62.22)	4.01(4.02)	2.87(2.96)	-	1585(1620)

[a] Calculated values are in parentheses. [b] The values of free ligands are in parentheses.

2.2. *IR and UV-vis spectra*

The chloro-complexes show a single sharp Ru–Cl stretch in the region 330–340 cm^{-1} which is absent for the bromo analogues (Table 1). The C=N stretches in the complexes display a significant shift ($\sim$ 40 cm^{-1}, Table 1) to lower frequencies compared with those for the free ligands, in accord with coordination of the azomethine function to the metal atom [15]. The OH stretch in the free ligands is observed as a prominent band in the region 3300–3360 cm^{-1}. This band is absent in Ru(RL)(PPh$_3$)$_2$X, as expected.

The complexes absorb moderately strongly in the visible region, with charge transfer bands in the regions 500–700 nm and 400–600 nm. Spectral data are listed in Table 2 and representative spectra are shown in Fig. 1.

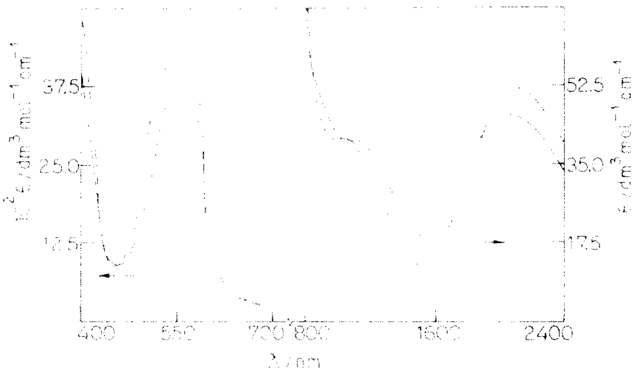


Fig. 1. Electronic spectra of **3** (———) and **4a** (— — —) in dichloromethane at 298 K.

2.3. *Magnetism, EPR and near-IR spectra*

The complexes are uniformly paramagnetic, with moments corresponding to one unpaired electron (low-spin d^5) (Table 3). Their X-band EPR spectra in a glassy 1 : 1 dichloromethane–toluene solution (77 K) is rhombic, with three distinct signals. Representative spectra of a chloro- and bromo-complex are shown in Fig. 2, and g values are listed in Table 3.

The EPR spectra were analysed using the g-tensor theory of low-spin d^5 ions [10,16–18]. Distortion from octahedral symmetry is expressed in the form of axial (Δ) and rhombic (V) components. The axial component can be assumed to be tetragonal (*trans*-Ru(PPh$_3$)$_2$ configuration, see below), resulting in splitting of the

TABLE 2. Electronic spectral data in dichloromethane solution

Compound	UV-vis and near-IR spectral data $\lambda_{\max}$ (nm) (ϵ (dm^3 mol^{-1} cm^{-1}))
1	2200(62), 1100 [a](57), 545(4800), 525(5000)
2	2200(44), 1000 [a](41), 555(2800), 530(3000)
3	2050(46), 1050 [a](41), 565(3500), 540(3500)
4	2200(50), 1150 [a](39), 565(3700), 545(3800)
5	2100(62), 1050 [a](87), 625(4700), 400 [a](7100)
1a	2050(44), 1150 [a](33), 540(3500), 520(3700)
2a	2150(48), 1150 [a](23), 565(3600), 545(3400)
3a	2050(54), 1100 [a](43), 565(3400), 540(3500)
4a	2100(52), 1150 [a](40), 565(4000), 545(4100)
5a	2050(57), 1150 [a](60), 625(4200), 405 [a](7300)

[a] Shoulder.

TABLE 3. Bulk magnetic moments in solid state at 298 K and EPR g values in 1 : 1 dichloromethane/toluene glass at 77 K

Compound	$\mu_{\rm eff}/\mu_{\rm B}$	g_1	g_2	g_3
1	1.90	2.378	2.107	1.933
2	1.94	2.348	2.110	1.936
3	1.93	2.348	2.110	1.933
4	1.95	2.358	2.113	1.927
5	1.91	2.360	2.113	1.929
1a	1.90	2.383	2.107	1.933
2a	1.94	2.362	2.111	1.937
3a	1.93	2.367	2.118	1.935
4a	1.95	2.365	2.117	1.936
5a	1.93	2.361	2.114	1.933

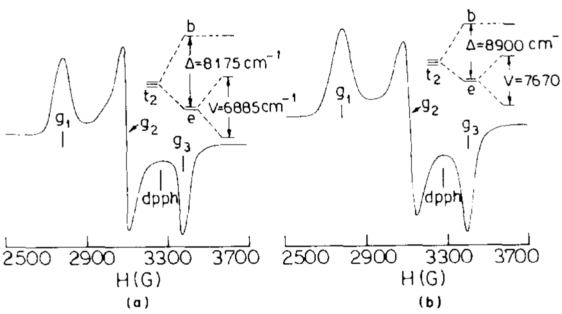


Fig. 2. X-band EPR spectra and t_2 splittings of (a) **4** and (b) **4a** in dichloromethane/toluene (1:1) glass (77 K).

octahedral t_2 shell into e + b. The superimposed rhombic distortion then splits e further into two non-degenerate components. This is shown in Fig. 2. Two ligand field transitions ν_1 and ν_2 among three Kramer's doublets are expected. Their energies, along with values of Δ and V calculated from the g parameters with the help of theory [10,16–18], are listed in Table 4. The value for the spin-orbit coupling constant of ruthenium(III) was taken as 1000 cm^{-1} [19,20].

The calculated values of ν_1 and ν_2 are ~5000 cm^{-1} and ~12000 cm^{-1}, respectively. The ν_1 band is observed in the expected region, 4500–4900 cm^{-1} (Tables 2 and 4, Fig. 1). In view of the approximations involved in the theory, the agreement between experimental and theoretical ν_1 values is excellent. Owing to the onset of strong absorption in the visible region, the ν_2 band is not clearly observed, but the weak shoulder near 1000 nm (Table 2, Fig. 1) may actually be a part of ν_2.

In summary, the $Ru(RL)(PPh_3)_2X$ complexes behave as model ruthenium(III) complexes possessing rhombic symmetry. The effective valence electron count of the coordinated metal ion is 17.

2.4. *Electrochemistry*

The redox behaviour of $Ru(RL)(PPh_3)_2X$ was examined voltammetrically in dichloromethane solution at a platinum electrode. Halfwave potential data (*vs.* SCE) are summarized in Table 5 and representative cyclic voltammograms are shown in Fig. 3. Two quasi-reversible responses (peak-to-peak separation ΔE_p 100–300 mV) were observed, and the separation between the two $E_{1/2}$ values was ~1.3 V. The one-electron nature of each couple was confirmed with the help of constant potential coulometry. Representative results are shown in Table 5.

TABLE 4. Distortion parameters and transition energies

Compound	Δ (cm^{-1})	V (cm^{-1})	ν_1 [a] (cm^{-1})	ν_2 (cm^{-1})
1	9039	8379	4951(4550)	13348
2	8833	7585	5136(4550)	12748
3	8576	7295	5026(4880)	12350
4	8175	6885	4834(4540)	11750
5	8347	7108	4893(4760)	12030
1a	9106	8529	4943(4880)	13490
2a	9090	8060	5156(4650)	13239
3a	8819	7572	5128(4880)	12728
4a	8903	7672	5162(4760)	12861
5a	8657	7441	5034(4880)	12502

[a] Experimental values are given in parentheses.

TABLE 5. Electrochemical data for dichloromethane solution at 298 K

Compound	Ru^{IV}–Ru^{III}			Ru^{III}–Ru^{II}		
	$E_{1/2}$ (V)	ΔE_p (mV)	n_1 [a]	$E_{1/2}$ (V)	ΔE_p (mV)	n_2 [b]
1	0.48	180	0.98	−0.81	160	0.96
2	0.51	180	0.97	−0.80	160	0.95
3	0.57	200	0.99	−0.76	180	0.98
4	0.60	170	1.01	−0.69	170	0.97
5	0.77	300	0.99	−0.57	300	1.02
1a	0.49	260	1.02	−0.81	160	0.97
2a	0.50	150	0.98	−0.80	150	0.96
3a	0.56	260	0.96	−0.78	250	1.01
4a	0.61	210	1.01	−0.67	190	0.97
5a	0.72	200	0.99	−0.55	210	0.98

[a] $n_1 = Q/Q'$, where Q' is the calculated coulomb count for 1e transfer and Q is the coulomb count found after exhaustive coulometric oxidation at +0.9 V. [b] $n_2 = Q/Q'$, where Q' is the calculated coulomb count for 1e transfer and Q is the coulomb count found after exhaustive coulometric reduction at −1.0 V.

The responses at negative (−0.5 to −0.8 V) and positive (0.4 to 0.8 V) potentials are respectively assigned to ruthenium(III)–ruthenium(II) and ruthenium(III)–ruthenium(IV) couples, as in eqns. (1) and (2). The free ligands do not display any redox activity

$$Ru^{III}(RL)(PPh_3)_2X + e^- \rightleftharpoons Ru^{II}(RL)(PPh_3)_2X^- \quad (1)$$

$$Ru^{IV}(RL)(PPh_3)_2X^+ + e^- \rightleftharpoons Ru^{III}(RL)(PPh_3)_2X \quad (2)$$

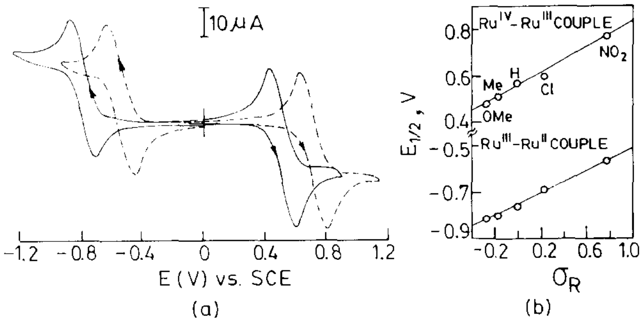


Fig. 3. (a) Cyclic voltammograms of **1a** (———) and **5a** (— — —) in dichloromethane (0.1 M TEAP). (b) Least-squares fit of $E_{1/2}$ *vs.* σ_R for species with X = Cl.

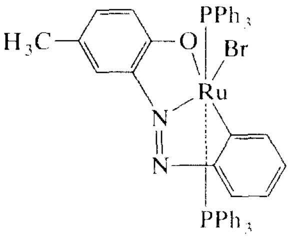
in the above potential ranges. The halfwave potentials are sensitive to the substituent R, and a plot of $E_{1/2}$ *vs.* σ_R is linear (Fig. 3), where σ_R is the Hammett constant of the substituent R.

The low reduction potentials of the ruthenium(III)–ruthenium(II) couple account for the fact that the trivalent complexes are formed when $Ru^{II}(PPh_3)_3X_2$ is treated with the Schiff bases under aerobic conditions. The bivalent complex, if formed initially, will be oxidized by aerial oxygen to the trivalent state. Thus when the coulometrically generated red solution of $Ru^{II}(RL)(PPh_3)_2X^-$ is exposed to air, rapid oxidation to stable $Ru^{III}(RL)(PPh_3)_2X$ occurs.

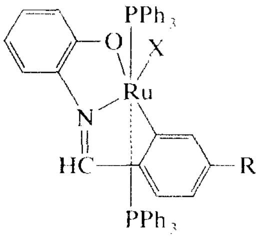
2.5. Comments on structure

We were unable to obtain suitable single crystals for X-ray characterization of any of the $Ru(RL)(PPh_3)_2X$ complexes. The complexes appear to be very crystalline, but the crystals are invariably twinned and several attempts at structure solution met with failure.

Elemental analyses and all other physical data are in agreement with the gross formulations **1**–**5**. Strong support for this is provided by the existence of azo analogues of $Ru(RL)(PPh_3)_2X$, one of which has been structurally characterized [10], revealing the geometry **6**. We suggest that $Ru(RL)(PPh_3)_2X$ has a similar geometry, **7**. The *trans* disposition of two PPh_3 ligands in complexes incorporating the $Ru^{III}(PPh_3)_2$ fragment is a general structural feature, and can be rationalized in terms of steric effects [21–24].



(6)



(7)

The EPR and electrochemical properties of $Ru(RL)(PPh_3)_2X$ are analogous to those of the azo species (type **6**). It is believed that the coordinated phenolate function plays an important role in making the ruthenium(III)–ruthenium(II) $E_{1/2}$ values low, which is crucial for the stability of the trivalent complexes under ambient conditions [10].

3. Experimental details

Commercial ruthenium trichloride (Arora Mathey, Calcutta, India) was purified by repeated evaporation to dryness with concentrated hydrochloric acid [25]. $Ru(PPh_3)_3Cl_2$ and $Ru(PPh_3)_3Br_2$ were prepared by a reported procedure [2]. All ligands were prepared by refluxing the substituted benzaldehyde with 2-aminophenol in ethanol. The purification of dichloromethane and the preparation of tetraethylammonium perchlorate for electrochemical/spectroscopic work were as described previously [18,22]. All other chemicals and solvents were of reagent grade and used without further purification.

UV-vis–near-IR spectra were recorded on a Hitachi 330 spectrophotometer and IR (4000–300 cm^{-1}) spectra (as KBr discs) on a Perkin-Elmer 783 spectrophotometer. The magnetic susceptibilities were measured on a PAR 155 vibrating-sample magnetometer. Electrochemical measurements were done with the PAR model 370-4 electrochemistry apparatus. The three-electrode measurements were carried out with a planar Beckman model 39273 platinum-inlay working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE). Tetraethylammonium perchlorate was the supporting electrolyte, and the solute concentration was ~ 10^{-3} mol dm^{-3}. The halfwave potential $E_{1/2}$ is set equal to $0.5(E_{pa}+E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials, respectively. The scan rate used was uniformly 50 mV s^{-1}. A platinum wire-gauze working electrode was used in coulometric experiments. All experiments were carried out under dinitrogen and the reported potentials are uncorrected for junction contribution. EPR measurements were made with a Varian model 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen). All spectra were calibrated by use of diphenylpicrylhydrazyl (dpph) ($g = 2.0037$). Microanalyses (C,H,N) were carried out with a Perkin-Elmer model 240C elemental analyser. The following Hammett σ values for *para* substituents were used: H, 0.00; Me, −0.17; OMe, −0.27; Cl, +0.23; NO_2, +0.78 [26].

3.1. Synthesis

Complexes were all made in yields of 80–85% by the same general procedures. Details are given for a representative example.

3.1.1. Chloro[2-(4′-methylbenzaldimine)phenolato-C$^{2'}$,N,O)]bis-(triphenylphosphine)ruthenium(III), (2)

A suspension of $Ru(PPh_3)_3Cl_2$ (0.10 g, 0.10 mmol) in 30 cm^3 of ethanol was warmed and 2-(4′-methylbenzaldimine)phenolate (0.30 g, 0.14 mmol) was added. The mixture was heated under reflux for 1 h then allowed to cool. A crystalline solid separated, and was filtered off and washed thoroughly with ethanol and then dried *in vacuo* over P_4O_{10}. It was then dissolved in a small volume of dichloromethane and chromatographed on an alumina column prepared in benzene. Elution with benzene gave a deep violet band, and evaporation afforded the crystalline complex in 84% yield.

Acknowledgements

We thank the Department of Science and Technology, and the Council of Scientific and Industrial Research, New Delhi, India, for financial support. Affiliation to the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India is acknowledged.

References

1 M.I. Bruce, *Comp. Organomet. Chem., 4* (1982) 651.
2 T.A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem., 28* (1966) 945.
3 J.V. Kingston and G. Wilkinson, *J. Inorg. Nucl. Chem., 28* (1966) 2709.
4 J. Halpern, B.R. James and A.L.W. Kemp, *J. Am. Chem. Soc., 88* (1966) 5142.
5 R. Colton and R.H. Farthing, *Aust. J. Chem., 24* (1971) 903.
6 M.L. Berch and A. Davison, *J. Inorg. Nucl. Chem., 35* (1973) 3763.
7 A.J. Hewitt, J.H. Holloway, R.D. Peacock, J.B. Raynor and I.L. Wilson, *J. Chem. Soc., Dalton Trans.* (1976) 579.
8 L.H. Pignolet and S.H. Wheeler, *Inorg. Chem., 19* (1980) 935.
9 M.M. Taqui Khan, D. Srinivas, R.I. Kureshy and N.H. Khan, *Inorg. Chem. 29* (1990) 2320.
10 G.K. Lahiri, S. Bhattacharya, M. Mukherjee, A.K. Mukherjee and A. Chakravorty, *Inorg. Chem., 26* (1987) 3359.
11 M. Ke, S.J. Rettig, B.R. James and D. Dolphin, *J. Chem. Soc., Chem. Commun.*, (1987) 1110.
12 J.W. Seyler and C.R. Leidner, *Inorg. Chem., 29* (1990) 3636.
13 M. Ke, C. Sishta, B.R. James, D. Dolphin, J.W. Sarapany and J.A. Ibers, *Inorg. Chem., 30* (1991) 4766.
14 M. Beley, J. Collin, R. Louis, B. Metz and J. Sauvage, *J. Am. Chem. Soc., 113* (1991) 8521.
15 M.M. Taqui Khan, N.H. Khan, R.I. Kureshy, A.B. Boricha and Z.A. Shaikh, *Inorg. Chim. Acta, 170* (1990) 213.
16 B. Bleaney and M.C.M. O'Brien, *Proc. Phys. Soc. London, Sect. B, 69* (1956) 1216.
17 J.S. Griffith, *The Theory of Transition Metal Ions*, Cambridge University Press, London, 1961, p. 364.
18 G.K. Lahiri, S. Bhattacharya, B.K. Ghosh and A. Chakravorty, *Inorg. Chem., 26* (1987) 4324.
19 N.J. Hill, *J. Chem. Soc., Faraday Trans. 2*, (1972) 427.
20 C. Daul and A. Goursot, *Inorg. Chem., 24* (1985) 3554.
21 A. Pramanik, N. Bag, G.K. Lahiri and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1990) 3823.
22 A. Pramanik, N. Bag, D. Ray, G.K. Lahiri and A. Chakravorty, *Inorg. Chem., 30* (1991) 410.
23 A. Pramanik, N. Bag, D. Ray, G.K. Lahiri and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, (1991) 139.
24 A. Pramanik, N. Bag, G.K. Lahiri and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1992) 101.
25 A.R. Chakravarty and A. Chakravorty, *Inorg. Chem., 20* (1981) 275.
26 L.P. Hammett, *Physical Organic Chemistry*, 2nd edition, McGraw-Hill, New York, 1970.