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Valence specific chelation of ruthenium to Schiff mono-bases of 2,6-diformyl-4-methylphenol: synthesis and structure of trivalent salicylaldiminato species of coordination type RuN_2O_2PCl

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Abstract—The reaction of Schiff mono-bases, HRL (R = Me, Et), of 2,6-diformyl-4-methylphenol with $K_2RuCl_5(H_2O)$ has afforded $Ru^{III}(RL)_2(PPh_3)Cl$. The X-ray structure of the R = Et complex has revealed metal chelation at the salicylaldimine segment of RL^-, the two phenolic oxygen and azomethine nitrogen atoms lying in mutually *trans* and *cis* positions, respectively. The trivalent state of the metal is stabilized in $Ru(RL)_2(PPh_3)Cl$, the ruthenium(III)/ruthenium(II) $E_{1/2}$ being ~0.40 V *vs* SCE. These distorted low-spin (t_2^5) complexes display rhombic EPR spectra and are characterized by a pair of ligand field transitions (in the near-IR region) within the split t_2 shell. The complexes provide a striking contrast with the ruthenium(II) organometallics arising from the reaction of HRL with $Ru^{II}(PPh_3)_3Cl_2$. © 1997 Elsevier Science Ltd

Keywords: trivalent ruthenium salicylaldimines; valence specific chelation.

The Schiff mono-base of 2,6-diformyl-4-methylphenol (**1**) is a potentially ambidentate chelate ligand with two possible binding sites: the salicylaldehyde site, A, and salicylaldimine site, B, the phenolic group being common to both. In the reaction of **1** with $Ru(PPh_3)_3Cl_2$, chelation associated with decarbonylation, is known to occur [1,2] at the A site as in motif **2**. We now report that it is the B site that is utilized, motif **3**, when **1** chelates ruthenium(III) in the presence of PPh_3. A remarkable valence specificity of the chelation mode of **1** is thus revealed. The synthesis as well as X-ray and electronic structures of complexes incorporating **3** are described. We have here the first structural characterization of a ruthenium(III) salicylaldiminate.

EXPERIMENTAL

Materials

The starting materials $K_2RuCl_5(H_2O)$ [3] and 2,6-diformyl-4-methylphenol [4] were prepared by reported procedures. The purification of dichloromethane and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were carried out as before [5]. All other chemicals and solvents were of analytical grade and used without further purification.

Preparation of complexes

The two $Ru(RL)_2(PPh_3)Cl$ complexes were prepared by the same procedure. Details are given below for the R = Et complex.

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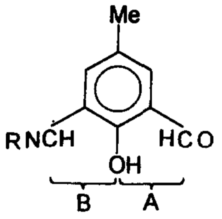

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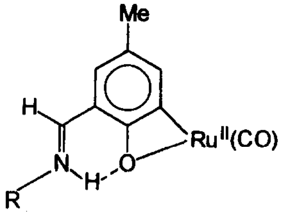

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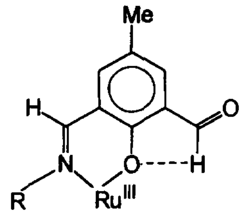

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Chloro-bis[4-*methyl*-6-*formyl*-2-(N-*ethyl*(*iminomethyl*)*phenolato*-N,O)]*triphenylphosphineruthenium* (III), Ru(EtL)$_2$(PPh$_3$)Cl. To a hot solution of 2,6-diformyl-4-methylphenol (54 mg, 0.33 mmol) in dehydrated ethanol (25 cm^3) was added a 50% aqueous solution of ethylamine (30 mg, 0.33 mmol EtNH$_2$). The mixture was heated for 20 min. To this hot yellow Schiff mono-base solution was successively added K$_2$RuCl$_5$(H$_2$O) (50 mg, 0.13 mmol) and PPh$_3$ (41 mg, 0.15 mmol). The reaction mixture was then heated to reflux until (~5 h) a deep green solution resulted. The ethanol solvent was removed under low pressure and the residue was purified by column chromatography on neutral Al$_2$O$_3$. The green Ru(EtL)$_2$(PPh$_3$)Cl complex was eluted with 1 : 1 benzene : acetonitrile. Yield: 70 mg [67% on the basis of K$_2$RuCl$_5$(H$_2$O)]. Found: C, 61.7; H, 5.1; N, 3.5. Calc. for C$_{40}$H$_{39}$N$_2$O$_4$PClRu: C, 61.6; H, 5.0; N, 3.6%.

Chloro-bis[4-*methyl*-6-*formyl*-2-(N-*methyl*(*iminomethyl*)*phenolato*-N,O)]*triphenylphosphineruthenium* (III), Ru(MeL)$_2$(PPh$_3$)Cl. This was similarly prepared using MeNH$_2$ in place of EtNH$_2$ in the above procedure. Yield: 65%. Found: C, 60.7; H, 4.7; N, 3.7. Calc. for C$_{38}$H$_{35}$N$_2$O$_4$PClRu: C, 60.7; H, 4.7; N, 3.7%.

Physical measurements

IR (4000–200 cm^{-1}) spectra (as KBr discs) were recorded on a Perkin–Elmer 783 spectrometer and electronic spectral measurements were made with a Hitachi 330 spectrophotometer. Magnetic susceptibilities were measured on a PAR 155 vibrating sample magnetometer and EPR spectra were obtained on a Varian model 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen). Spectra were calibrated with diphenylpicrylhydrazyl (DPPH), g = 2.0037. Electrochemical measurements were performed under nitrogen atmosphere on a PAR model 370-4 electrochemistry apparatus as reported earlier [5]. Microanalyses (C,H,N) were carried out with a Perkin–Elmer 240C elemental analyser. Solution (~10^{-3} M) electrical conductivities were measured with the help of a Philips PR 9500 bridge.

X-ray structure determination of Ru(EtL)$_2$(PPh$_3$)Cl

A single crystal of $0.24 \times 0.36 \times 0.22$ mm^3 grown (at 298 K) by slow diffusion of hexane into dichloromethane solution was used. Cell parameters were determined by least-squares fit of 30 machine-centered reflections (2θ = 14–28°). Data were collected by the ω-scan technique in the angle $3 \leqslant 2\theta \leqslant 48°$ on a Siemens R3m/V four-circle diffractometer with the graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction. All data were corrected for Lorentz–polarization effects and an empirical absorption correction was done on the basis of azimuthal scan of five reflections [6].

Systematic absences led to the space group $P2_1/n$. The metal atom was located from Patterson maps and the remaining non-hydrogen atoms emerged from successive Fourier synthesis. The structure was refined by full-matrix least-square procedure. All non-hydrogen atoms except PPh$_3$ carbons were refined anisotropically. The methyl carbon [C(29)] of the N(1)Et substituent shows two fold disorderness around the C(28)–C(29) bond. A number of hydrogen atoms [H(21), H(23), H(26), H(27), H(32), H(34) and H(37)] were directly located from difference-Fourier maps and others were added at calculated positions with fixed U = 0.08 Å^2. The aldehydic hydrogens [H(26) and H(37)] were refined isotropically. The highest residual was 0.43 e Å^{-3}. All calculations were done on a Micro VaxII computer using the SHELXTL-PLUS program package [7]. Significant crystal data are listed in Table 1.

Tables of atomic coordinates, anisotropic thermal parameters, full listings of bond lengths and angles, and observed and calculated structure factors are available as supplementary materials from the Editor.

RESULTS AND DISCUSSION

Synthesis and valence specificity of chelation

Two Schiff bases of type **1** abbreviated as HRL (R = Me, Et), have been used. The most convenient ruthenium(III) salt for synthesis has been found to be

Table 1. Crystal data collection and refinement parameters for $Ru(EtL)_2(PPh_3)Cl$

Molecular formula	$C_{40}H_{39}N_2O_4PClRu$
Molecular weight	778.84
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	18.194(10)
b (Å)	9.164(4)
c (Å)	23.697(12)
β (°)	106.24(4)
V (Å^3)	3793(3)
Z	4
D_c (g cm^{-3})	1.364
μ (Mo-K_α) (cm^{-1})	5.67
Temperature (°C)	22
Transmission coefficient	0.8052–0.9122
Total no. of reflections	6833
No. of unique reflections	6159
No. of observed reflections [$I > 3.0\sigma(I)$]	2216
No. of parameters refined	368
Final R^a	0.0538
Final $R_w{}^b$	0.0571
Goodness of fit (GOF)^c	1.12

[a] $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$.

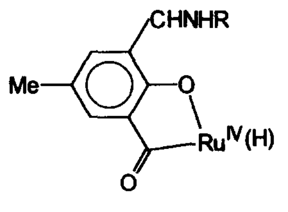
[b] $R_w = [\Sigma w(\|F_o| - |F_c\|)^2 / \Sigma w |F_o|^2]^{1/2}$.

$w^{-1} = \sigma^2|F_o| + g|F_o|^2$, $g = 0.0008$.

[c] The GOF is defined as $[\Sigma w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the number of data and variables, respectively.

$K_2RuCl_5(H_2O)$. It reacts with HRL in the presence of PPh_3 affording deep green $Ru^{III}(RL)_2(PPh_3)Cl$ in good yield. The complexes display C═O, C═N an Ru—Cl stretches at 1670, 1540 and 325 cm^{-1} respectively.

The reaction of $Ru^{II}(PPh_3)_3Cl_2$ with **1** proceeds *via* oxidative addition, the probable intermediate being **4**, which is subject to rearrangement and reductive proton elimination affording motif **2** [1,2]. When the starting material is $K_2Ru^{III}Cl_5(H_2O)$, the trivalent metal is unsuitable for oxidative addition and instead gets O,N-chelated at the salicylaldimine site. The salicylaldehyde site is a potential O,O-chelator [8], but in practice the stronger O,N-chelation prevails.



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Geometry and bond parameters

The X-ray structure of $Ru(EtL)_2(PPh_3)Cl$ has been determined. A view of the molecule is shown in Fig. 1 and selected bond parameters are set out in Table 2. Both the EtL ligands are bonded as in motif **3**. The two phenolic oxygens lie *trans* to each other while the azomethine nitrogen atoms span *cis* positions in the distorted octahedral RuO_2N_2PCl coordination sphere. The six-membered RuC_3NO chelate rings are not quite planar due to a deviation (by 0.5–0.6 Å) of the metal atom from the excellent C_3NO plane (mean deviation, ~0.02 Å).

No other Ru^{III}-salicylaldimine species appear to have been structurally characterized and length data on authentic Ru^{III}—O bonds are rare [5,8]. The average distance in the present complex, 1.992(7) Å, compares well with that 1.981(2) Å in tris(salicylaldehydato)-ruthenium(III) [8]. In the few known [9] Ru^{II}-salicylaldimine structures, Ru^{II}—O lengths span the range 2.03–2.08 Å reflecting the increase of metal radius upon reduction. The *trans* influence [10] of PPh_3 in $Ru(EtL)_2(PPh_3)Cl$ is seen in the longer (by 0.06 Å) Ru—N(2) bond (*trans* ligand is PPh_3) compared with the Ru—N(1) bond (*trans* ligand is Cl).

A number of hydrogen atoms in the structure were directly located and these include the two aldehyde hydrogen atoms which were refined isotropically ($U = 0.08$ Å^2). The O(1), C(19), C(24), C(26) and H(26) atoms make an excellent plane (mean deviation 0.03 Å). The same applies to O(3), C(30), C(35), C(37) and H(37). The aldehyde C—H lengths are nearly equal to 1.1(1) Å. The average distance between the phenolic oxygen and aldehyde hydrogen atoms is 2.5(1) Å, suggesting the presence of weak CH···O hydrogen bonding as depicted in **3**. In contrast motif **2** is characterized by relatively stronger N—H···O hydrogen bonding between iminium hydrogen and phenolato oxygen [1,2].

Electronic structure

The complexes behave as one-electron paramagnets ($s = 1/2$) corresponding to the low-spin $d^5(t_2^5)$ configuration and are EPR-active (Table 3). The EPR spectra in frozen dichloromethane–toluene glass (77 K) are rhombic (Fig. 2) consistent with the X-ray structural geometry (C_1 symmetry). The spectra have been analysed using g-tensor theory [5,11,12] of low-spin d^5 ions (Table 3). The axial distortion (Δ) splits the t_2 shell into $e + b$ levels and the rhombic distortion (V) splits e further into two nondegenerate components (Fig. 2). Setting λ, the spin-orbit coupling constant of ruthenium(III), as 1000 cm^{-1} [13], two ligand field transitions are predicted near 4000 and 8500 cm^{-1} within the Kramers doublets (Table 3). The complexes indeed display two low intensity bands in the near-IR region at ~4500 and ~6500 cm^{-1} in

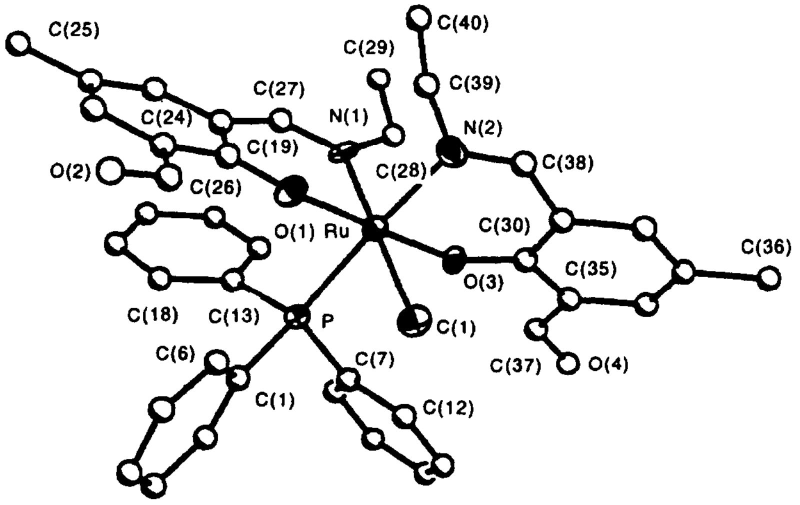

Fig. 1. Perspective view and atom labeling scheme for $Ru(EtL)_2(PPh_3)Cl$.

Table 2. Selected bond distances (Å) and angles (°) and their estimated standard deviations for $Ru(EtL)_2(PPh_3)Cl$

Ru—Cl	2.385(4)	Ru—P	2.375(3)
Ru—O(1)	1.999(7)	Ru—O(3)	1.986(7)
Ru—N(1)	2.036(9)	Ru—N(2)	2.099(10)
Cl—Ru—P	90.2(1)	Cl—Ru—O(1)	89.3(2)
P—Ru—O(1)	93.7(2)	Cl—Ru—O(3)	90.4(3)
P—Ru—O(3)	88.7(2)	O(1)—Ru—O(3)	177.6(3)
O(1)—Ru—N(1)	89.6(3)	O(3)—Ru—N(2)	89.3(3)
Cl—Ru—N(1)	178.3(3)	P—Ru—N(1)	91.2(3)
Cl—Ru—N(2)	85.9(3)	P—Ru—N(2)	175.6(3)
O(1)—Ru—N(2)	88.3(3)	O(3)—Ru—N(1)	90.7(3)
N(1)—Ru—N(2)	92.7(4)		

Table 3. Magnetic moment in the solid state (298 K), EPR g values in 1 : 1 dichloromethane/toluene glass (77 K), distortion parameters and transition energies

	μ_{eff}[a]	g_1	g_2	g_3	Δ/λ	V/λ	ν_1/λ	ν_2/λ
$Ru(EtL)_2(PPh_3)Cl$	1.90	2.364	2.106	1.878	5.966	−4.587	3.805 (4.4)[b]	8.443 (6.7)[b]
$Ru(MeL)_2(PPh_3)Cl$	1.89	2.363	2.113	1.883	6.078	−4.577	3.917 (4.4)[b]	8.546 (6.2)[b]

[a] B.M.

[b] Experimental values.

addition to the intense LMCT band near 16,000 cm^{-1} (Table 4, Fig. 3). In view of the many approximations involved in the theory, the agreement between calculated and experimental near-IR transition energies is quite satisfactory.

Metal redox

Bis-salicylaldiminato binding excellently stabilizes the trivalent state. This is reflected in the low ruthenium(III)/ruthenium(II) reduction potential (~ −0.4 V *vs* SCE, Table 4) of the quasireversible (ΔE_p = 100 mv) cyclic voltammetric couple of eq. (1). The

$$\mathrm{Ru^{III}(RL)_2(PPh_3)Cl + e \rightleftharpoons Ru^{II}(RL)_2(PPh_3)Cl^-} \qquad (1)$$

corresponding ruthenium(IV)/ruthenium(III) couple is observed near ~0.9 V.

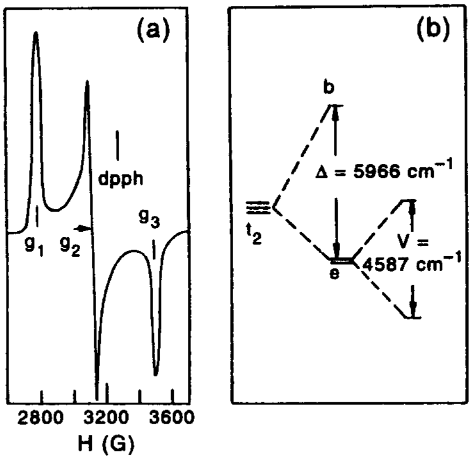

Fig. 2. (a) X-band EPR spectrum in dichloromethane-toluene (1 : 1) glass (77 K) and (b) t_2 splittings of Ru(EtL)$_2$(PPh$_3$)Cl.

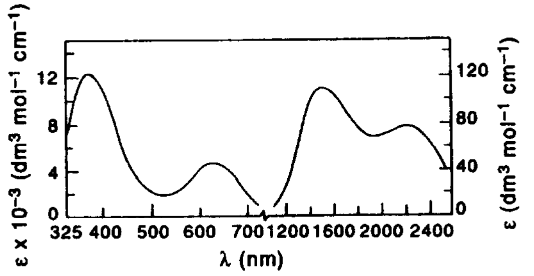

Fig. 3. Electronic spectrum of Ru(EtL)$_2$(PPh$_3$)Cl in dichloromethane.

The complexes incorporating motif **2** are of type Ru(RL′)(PPh$_3$)$_2$(CO)Cl, where Ru(RL′)(CO) is motif **2**. Here the ruthenium(II) state is stabilized, the ruthenium(III)/ruthenium(II) reduction potential being ~0.5 V [2]. In this case the ruthenium(III) congeners are inherently unstable and could not be isolated.

CONCLUSION

It is shown that the Schiff mono-bases of 2,6-diformyl-4-methylphenol, HRL (R = Et, Me), **1**, react with $K_2RuCl_5(H_2O)$ affording ruthenium(III)-salicylaldimine complexes of the type Ru^{III}(RL)$_2$(PPh$_3$)Cl in which the aldehyde functions remain uncoordinated. The system provides a remarkable valence specific contrast with the ruthenium(II) organometallic species (motif **2**) formed from the reaction of **1** with Ru^{II}(PPh$_3$)$_3$Cl$_2$. Ru(EtL)$_2$(PPh$_3$)Cl represents the first case of structural characterization of a ruthenium(III)-salicylaldimine species. The two phenolic oxygen atoms and the two azomethine nitrogen atoms are respectively coordinated in mutually *trans* and *cis* positions. The PPh$_3$ molecule exerts significant trans influence on a Ru—N bond. The Ru^{III}(RL)$_2$(PPh$_3$)Cl species display highly rhombic EPR spectra consistent with large axial and rhombic distortions. Predicted near-IR transitions without the Kramers doublets are observed experimentally. The complexes have relatively low metal redox potentials corresponding to stabilization of the ruthenium(III) state.

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Table 4. Electronic spectral and electrochemical data

Compound	Electronic spectra^a λ_{max}, nm (ε^b, dm^3 mol^{-1} cm^{-1})	Electrochemical data^c [$E_{1/2}$, V (ΔE_p, mV)] Ru^{III}/Ru^{II}	 Ru^{IV}/Ru^{III}
Ru(EtL)$_2$(PPh$_3$)Cl	2250(80), 1500(110) 630(4840), 365(12,320)	−0.41(100)	0.95(100)
Ru(MeL)$_2$(PPh$_3$)Cl	2260(60), 1620(150) 620(3720), 365(11,780)	−0.51(120)	0.93(120)

^{a} Solvent is dichloromethane.

^{b} Extinction coefficient.

^{c} Conditions: solvent, dichloromethane; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, ~10^{-3} M; $E_{1/2} = 0.5(E_{pa}+E_{pc})$ at scan rate 50 mV s^{-1}, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa}-E_{pc}$.

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