

Paramagnetic ruthenium(III) cyclometallated complex. Synthesis, spectroscopic studies and electron-transfer properties

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Abstract

The reaction of $\text{Ru}^{\text{II}}(\text{PPh}_3)_3\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) with $o\text{-(OH)C}_6\text{H}_4\text{C(H)=N-CH}_2\text{C}_6\text{H}_5$ (HL) under aerobic conditions affords $\text{Ru}^{\text{II}}(\text{L})_2(\text{PPh}_3)_2$, **1**, in which both the ligands (L) are bound to the metal center at the phenolic oxygen (deprotonated) and azomethine nitrogen and $\text{Ru}^{\text{III}}(\text{L}^1)(\text{L}^2)(\text{PPh}_3)$, **2**, in which one L is in bidentate N,O form like in complex **1** and the other ligand is in tridentate C,N,O mode where cyclometallation takes place from the *ortho* carbon atom (deprotonated) of the benzyl amine fragment. The complex **1** is unstable in solution, and undergoes spontaneous oxidative internal transformation to complex **2**. In solid state upon heating, **1** initially converts to **2** quantitatively and further heating causes the rearrangement of complex **2** to the stable RuL_3 complex. The presence of symmetry in the diamagnetic, electrically neutral complex **1** is confirmed by ^1H and ^{31}P NMR spectroscopy. It exhibits an $\text{Ru}^{\text{II}} \rightarrow \text{L}$, MLCT transition at 460 nm and a ligand based transition at 340 nm. The complex **1** undergoes quasi-reversible ruthenium(II)–ruthenium(III) oxidation at 1.27 V vs. SCE. The one-electron paramagnetic cyclometallated ruthenium(III) complex **2** displays an $\text{L} \rightarrow \text{Ru}^{\text{III}}$, LMCT transition at 658 nm. The ligand based transition is observed to take place at 343 nm. The complex **2** shows reversible ruthenium(III)–ruthenium(IV) oxidation at 0.875 V and irreversible ruthenium(III)–ruthenium(II) reduction at -0.68 V vs. SCE. It exhibits a rhombic EPR spectrum, that has been analysed to furnish values of axial (6560 cm^{-1}) and rhombic (5630 cm^{-1}) distortion parameters as well as the energies of the two expected ligand field transitions (3877 cm^{-1} and 9540 cm^{-1}) within the t_2 shell. One of the transitions has been experimentally observed in the predicted region (9090 cm^{-1}). The first order rate constants at different temperatures and the activation parameter $\Delta H^\ddagger/\Delta S^\ddagger$ values of the conversion process of **1** $\rightarrow$ **2** have been determined spectrophotometrically in chloroform solution. © 1997 Elsevier Science S.A.

Keywords: Ruthenium; Electron-transfer

1. Introduction

Although variable valence properties pervade the chemistry of ruthenium, cyclometallated complexes are primarily restricted to the diamagnetic bivalent ruthenium(II) oxidation state [1–17]. Paramagnetic ruthenium(III) organometallic systems are scarce in spite of the tremendous growth of the coordination chemistry of trivalent ruthenium [18]. Only few authentic examples of paramagnetic ruthenium(III) organometallics are known in the literature up to now [19–34].

The present work originates from our interest in developing new paramagnetic trivalent ruthenium cyclometallated complexes. Herein we report the synthesis

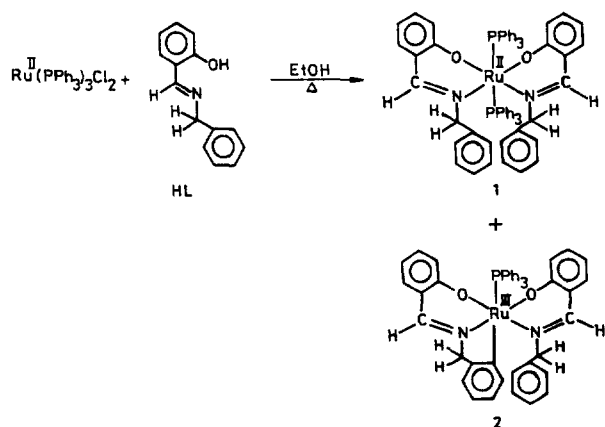
of one such complex, $\text{Ru}^{\text{III}}(\text{C,N,O})(\text{N,O})(\text{PPh}_3)$ (**2**) in a mixed phenolato-imine and phosphine ligand environment as a direct product from the initial reaction of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ and HL (Scheme 1) as well as from the internal conversion of a non-cyclometallated complex $\text{Ru}^{\text{II}}(\text{N,O})_2(\text{PPh}_3)_2$ (**1**) both in solution and in solid state. Spectroscopic characterization, electron-transfer properties, kinetics and thermodynamic properties and the determination of the electronic structure of the complex have been reported.

2. Results and discussion

2.1. Synthesis and characterization of the complexes

The reaction of the suspension of $\text{Ru}^{\text{II}}(\text{PPh}_3)_3\text{Cl}_2$ in ethanol with the ligand (HL) $o\text{-(OH)C}_6\text{H}_4\text{C(H)=N-}$

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Scheme 1.

$\text{CH}_2\text{C}_6\text{H}_5$ in the ratio 1:2 under reflux conditions results in an orange solution from which the orange solid separates out immediately. The solution is gradually turned to deep green over a period of 4 h. The complex **1** is obtained as a fine orange solid in pure form after filtration of the reaction mixture followed by thorough washing with ethanol and diethylether. On removal of the solvent from the green filtrate part under reduced pressure the crude deep green solid results. Chromatographic purification of the crude green solid on an alumina column using CHCl_3 as eluent yields the pure dark green solid **2** (Scheme 1).

Identical products, complexes **1** and **2**, have also been achieved starting from $\text{Ru}^{\text{II}}(\text{PPh}_3)_3\text{Br}_2$ instead of $\text{Ru}^{\text{II}}(\text{PPh}_3)_3\text{Cl}_2$ which supports the absence of any coordinated halide group in the complexes (**1** and **2**).

The complex **1** is highly soluble only in non-polar solvents such as benzene, dichloromethane, chloroform and slightly in N,N -dimethylformamide. At room temperature the complex **1** is very much stable in solid state but in solution it transforms quantitatively to complex **2**. Complex **2** is highly soluble in both polar (acetonitrile, alcohol, N,N -dimethyl formamide, dimethylsulfoxide) and non-polar (dichloromethane, chloroform, benzene, ether, hexane, etc.) solvents, but not in water.

The conductivity measurements of the complex **1** in DMF and the complex **2** in DMF, CH_3CN and MeOH indicate that both the complexes are electrically non-conducting. Solid state magnetic moment measurements at 298 K suggest that the complex **1** is diamagnetic (low-spin, Ru^{II} , t_{2g}^6 , $S = 0$) and the complex **2** is paramagnetic with magnetic moment ($\mu = 1.89 \text{ B.M.}$) corresponding to one unpaired electron (low-spin, Ru^{III} , t_{2g}^5 , $S = 1/2$). Microanalytical data (C, H, N) of the complexes are in good agreement with the calculated values (see Section 4), thus confirming the compositions of the complexes **1** and **2**.

2.2. IR spectra

IR spectra of the complexes (**1** and **2**) are recorded as KBr discs. Both the spectra exhibit several intense bands. No attempt has been made to assign all the bands except the few characteristic vibrations. The $\nu(\text{C}=\text{N})$ stretching frequency of the free ligand (L) appears at 1628 cm^{-1} , which has been shifted to 1590 cm^{-1} and 1600 cm^{-1} in complexes **1** and **2** respectively in accord with coordination of the azomethine function to the metal atom [35]. Phosphine vibrations for the complexes (**1** and **2**) appear around 700 and 520 cm^{-1} [36]. The O–H stretch in the free ligand is observed as a prominent band at 3390 cm^{-1} . This band is absent in the complexes as expected. Since no Ru–Cl or Ru–Br vibration is observed for both the complexes, the possibility of any coordinated chloride or bromide in the complexes can therefore be ruled out.

2.3. UV–visible spectra

UV–visible spectra of the complexes (**1** and **2**) are recorded in chloroform solvent. Spectra are shown in Fig. 1. Since complex **1** is unstable in solution, the

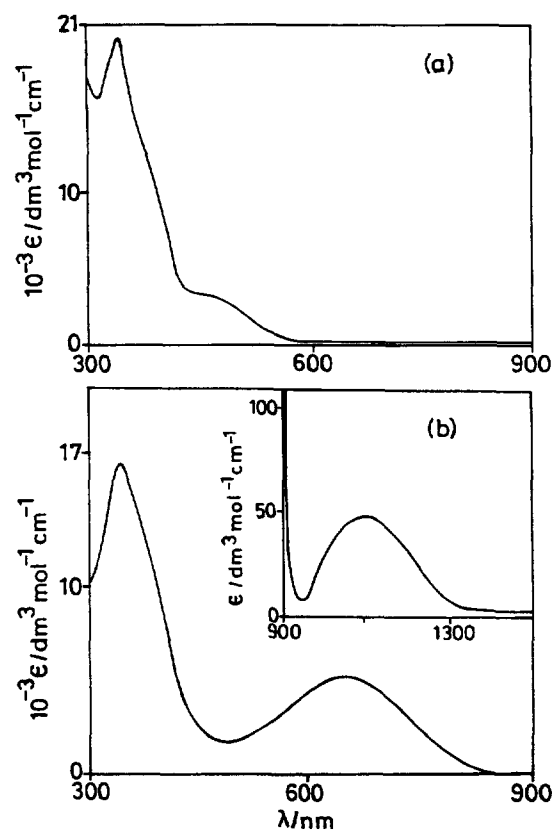


Fig. 1. (a) Electronic spectrum of **1** in chloroform at 298 K. (b) Electronic spectrum of **2** in chloroform at 298 K. Inset: electronic spectrum of **2** in the range 1500–900 nm.

freshly prepared quantitative solution of **1** in CHCl_3 is used to record the spectrum immediately. It displays one moderately intense band at 460 nm (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$; 3125) and a strong band at 340 nm (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$; 20536) (Fig. 1(a)). The lowest energy band at 460 nm is assigned to the $\text{Ru}^{\text{II}} \rightarrow$ ligand charge-transfer transition (MLCT) [31,33] and the higher energy intense band at 340 nm may be due to a ligand based transition. The complex **2** exhibits one moderately intense slightly broad band at 658 nm (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$; 4900) and a sharp intense band at 343 nm (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$; 16500) (Fig. 1(b)). The lowest energy band at 658 nm may be due to a ligand $\rightarrow \text{Ru}^{\text{III}}$ charge-transfer transition (LMCT) [34,35] and the intense band at 343 nm is believed to be due to a ligand based transition.

2.4. ^1H NMR spectra

^1H NMR spectra of the free ligand (HL) and the complex **1** are recorded in CDCl_3 solvent. The spectra are shown in Fig. 2. For free ligand the azomethine proton ($-\text{CH}=\text{N}-$) and the methylene protons ($-\text{CH}_2-$) appear as a singlet at 8.43 and 4.80 ppm respectively. The O–H proton appears as a broad peak at 13.42 ppm

as expected. Seven out of nine aromatic protons give rise to a complex pattern centered at 7.3 ppm and the other two protons are observed as a doublet (6.96 ppm) and a triplet (6.88 ppm) (Fig. 2(a)).

The ^1H NMR spectrum of the complex **1** is complicated in the region 6–8 ppm due to the presence of too many protons of the phenyl rings of phosphine and the ligand (L). However, the CH_2 protons are observed as a doublet of doublets centered at 4.91 ppm. The absence of the $-\text{OH}$ proton of the free ligand (HL) in the spectrum of complex **1** (Fig. 2(b)) suggests coordination through the phenolato oxygen. Aromatic protons have appeared as two complex signals centered at 7.62 and 7.02 ppm. A direct comparison of the intensity of the aromatic protons with that of the methylene protons (δ , 4.9 ppm) reveals the presence of 25 aromatic protons corresponding to one ligand (L) and one phosphine. This is possible only when there is symmetry in the molecule such that half of the molecule is representing the other half. However, at present it is not possible to assign unambiguously the configuration of **1** as *cis-trans-cis* or *trans-trans-trans* with respect to phenolato oxygens, triphenyl phosphines and imine nitrogens.

Since the diamagnetic Ru^{II} complex **1** in solution undergoes oxidative transformation to the paramagnetic Ru^{III} complex **2**, the solution of complex **1** is prepared under N_2 atmosphere and the spectrum is immediately recorded. The signals start broadening with time due to the formation of paramagnetic complex **2** at the expense of diamagnetic complex **1**, and ultimately it gives a very broad spectrum which is identical with the spectrum obtained directly from the isolated paramagnetic complex **2** in CDCl_3 solution.

2.5. ^{31}P NMR spectra

^{31}P NMR spectra of the complexes **1** and **2** are recorded in CDCl_3 solvent. Complex **1** displays one sharp signal at 32.772 ppm, implying the presence of a *trans* configuration of the two phosphines in the complex **1** as opposed to the *cis* form. A *trans* configuration of the $\text{Ru}(\text{PPh}_3)_2$ core is also expected from the steric point of view [37]. A phosphine signal for the complex **2** is observed at 30.011 ppm.

2.6. Electron-transfer properties

Electron-transfer properties of the complexes **1** and **2** have been studied in dichloromethane solution by cyclic voltammetry (CV) using a platinum working electrode. Complexes are electroactive with respect to the metal center in the potential range ± 1.5 V vs. SCE (tetraethyl ammonium perchlorate is used as electrolyte, 298 K). Voltammograms are shown in Fig. 3. The complex **1** exhibits one quasi-reversible response at E_{298}° , 1.27 V (peak to peak separation ΔE_p , 110 mV). The anodic and

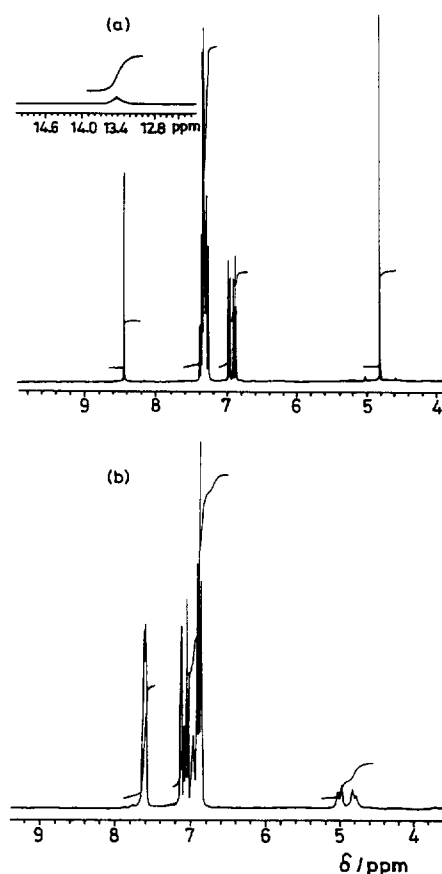


Fig. 2. (a) ^1H NMR spectrum of HL in CDCl_3 . (b) ^1H NMR spectrum of **1** in CDCl_3 .

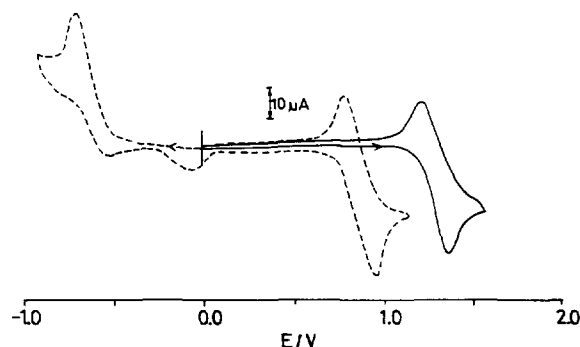
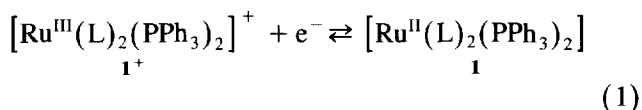


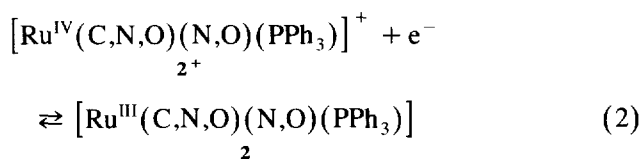
Fig. 3. Cyclic voltammograms of **1** (—) and **2** (---) in dichloromethane.

cathodic current heights are equal and vary as the square root of the scan rate. This reversible process is assigned to a ruthenium(II)–ruthenium(III) oxidation couple, Eq. (1).



The one-electron nature of the couple is confirmed by the current height consideration. As the complex **1** is unstable in solution, the complex is therefore dissolved in dichloromethane solvent under nitrogen atmosphere and the voltammogram is recorded immediately. With time gradually the solution changes to a bluish green color and displays the voltammogram corresponding to the complex **2** (see below).

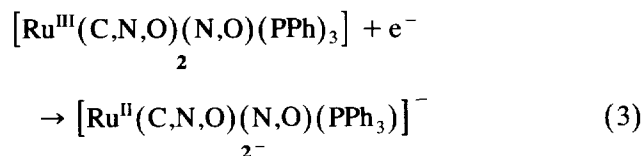
The cyclic voltammograms of the complex **2** display one quasi-reversible oxidative couple at E_{298}° , 0.875 V (peak to peak separation ΔE_p , 120 mV) and an irreversible reductive response at E_{pc} , -0.68 V. The potential separation between the two responses is ~ 1.5 V. The one-electron nature of the quasi-reversible couple at the positive side of the SCE is confirmed with the help of constant potential coulometry ($n = 0.97$ where $n = Q/Q'$, Q' is the calculated coulomb count for one-electron transfer and Q is the coulomb count found after exhaustive electrolysis). The oxidized solution 2^+ shows the cyclic voltammogram which is superposable to that of the starting reduced solution **2**, suggesting that the oxidation process here may be stereoretentive in nature. This oxidation process is assigned to a ruthenium(III)–ruthenium(IV) process (Eq. (2)).



Although the tetravalent congener of **2** can be generated in solution by bulk electrolysis, the 2^+ species is unstable at room temperature. This has precluded the

isolation and the further characterization of the hitherto unknown tetravalent cyclometallated complex under the present ligand set up.

The one-electron nature of the irreversible response at the negative side of the SCE is established by comparing the current height E_{pc} of this response with the current height of the experimentally established one-electron ($\text{Ru}^{\text{III}} \rightarrow \text{Ru}^{\text{IV}}$) process occurring at the positive side of the SCE (Eq. (2)). This irreversible reductive process is assigned to ruthenium(III) $\rightarrow$ ruthenium(II) reduction (Eq. (3)).



The 1.5 V potential separation between the two successive redox processes, Eqs. (2) and (3), is in very good agreement with the observed average potential difference between the $\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}}$ – $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ couples (1.3–1.6 V) in mononuclear ruthenium complexes having C,N,O, and thioether donor centers [31,34,35,38–40].

The free ligand (HL) does not show any redox activity within the above potential range. In the complex **1** where the two phosphines and two bidentate N,O coordinating ligands (L) are present, the ruthenium(II) $\rightarrow$ ruthenium(III) oxidation process takes place at very high potential, 1.27 V. The same ruthenium(II) $\rightarrow$ ruthenium(III) oxidation potential is observed near -0.6 V for the complex **2**. This huge negative shift of Ru^{II} to Ru^{III} oxidation potential on going from complex **1** to **2** is due to the replacement of a π -acceptor PPh_3 ligand by a strong σ -donor metal–carbon bond [41].

2.7. EPR, near-IR spectra and electronic structure

The one-electron paramagnetic complex **2** consists of two ligands (L) (one in bidentate N,O and the other in tridentate C,N,O coordinating mode) and one triphenyl phosphine ligand. Under the present octahedral Ru^{III} asymmetric ligands arrangement, a rhombic EPR spectrum is expected. The X-band EPR spectrum of the complex **2** is recorded in a glassy 1:1 chloroform–toluene (77 K). The spectrum is shown in Fig. 4. The observed EPR spectrum is indeed highly rhombic in nature with three distinct g values, $g_1 = 2.361$, $g_2 = 2.089$ and $g_3 = 1.889$.

The theory of EPR spectra of distorted octahedral low-spin d^5 (idealized t_{2g}^5 ground term $^2T_{2g}$) complexes is documented in the literature [31,33–38,42–45]. The distortion of pseudo-octahedral complexes can be expressed as the sum of axial (Δ) and rhombic (V) components. The t_2 orbital consists of the components

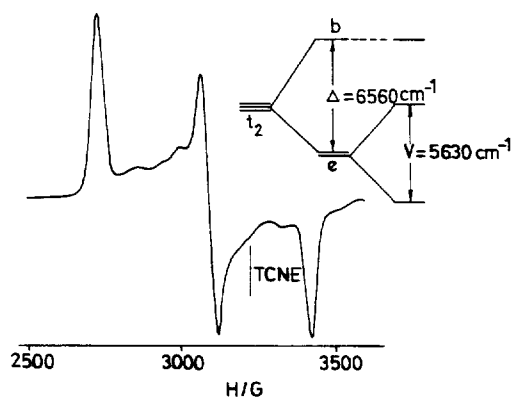


Fig. 4. X-band EPR spectrum and t_2 splittings of **2** in chloroform/toluene (1:1) glass (77 K).

$t_2^0(xy)$, $t_2^+(xz)$ and $t_2^-(yz)$ [42–45]. The degeneracy of the t_2 orbital is partially removed by axial distortion (Δ), which places $t_2^0(b)$ above $t_2^+(t_2^-)(e)$. The superimposed rhombic distortion (V) then splits (e) further into t_2^+ and t_2^- .

The analysis of the EPR spectrum using the g -tensor theory of low-spin d^5 ions provides the distortion parameters (Δ and V) of the complex and the energies of two crystal field transitions (ν_1 and ν_2) which arise due to optical transitions from ground to upper Kramers doublets [31].

The ESR experiment gives only the absolute g values and so neither their signs nor the correspondence of g_1 , g_2 or g_3 , to g_x , g_y or g_z are known. There are 48 possible combinations based on the labeling (x, y, z) and signs chosen for the experimentally observed g values. In the present complex we have chosen the combination where g_1 and g_2 are negative, g_3 is positive and the order of magnitude $g_1 > g_2 > g_3$ at this particular combination gives a reasonable value of k (orbital reduction factor) (< 1.0). The value of k for all other combinations of g parameters does not fall within the limit ($k < 1.0$), and is therefore rejected. The resulting values of orbital reduction factor (k), axial distortion (Δ), rhombic distortion (V) and the two ligand field transitions (ν_1 and ν_2) for the complex **2** are 0.695, 6560 cm^{-1} , 5630 cm^{-1} , 3877 cm^{-1} and 9540 cm^{-1} respectively. The value for the spin-orbit coupling constant (λ) of the ruthenium(III) is taken as 1000 cm^{-1} [40].

Experimentally by near-IR spectra the ν_2 band is observed in the expected position, 9090 cm^{-1} (ϵ ,

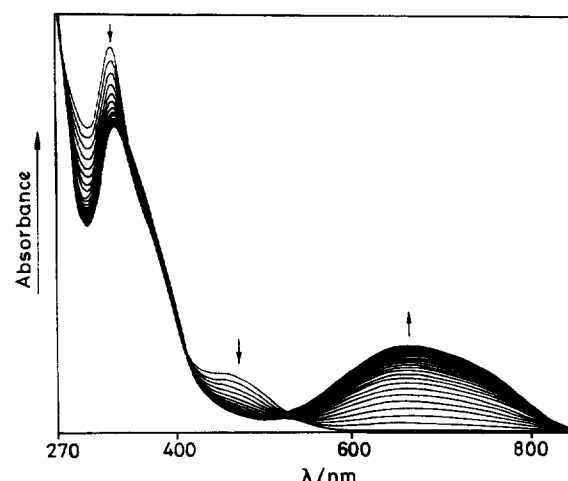


Fig. 5. Time evolution of the electronic spectra of a changing solution of complex **1** in chloroform at 301 K. The arrows indicate increase or decrease in band intensities as the reaction proceeds.

$\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$; 48) (Fig. 1(b)). In view of the approximation involved in the theory, the agreement between the experimentally observed ν_2 and the calculated ν_2 value is excellent. Due to the instrumental wavelength scan limitation (maximum up to 2200 nm) it has not been possible to check the ν_1 band properly. However, the increase of absorption starting further from 2000 nm is a clear indication of the presence of a ν_1 band near the calculated position.

The complex **1** is diamagnetic and EPR inactive. In solution, complex **1** gradually turns into the paramagnetic complex **2** and displays an EPR spectrum identical to the EPR spectrum obtained from the isolated pure complex **2**.

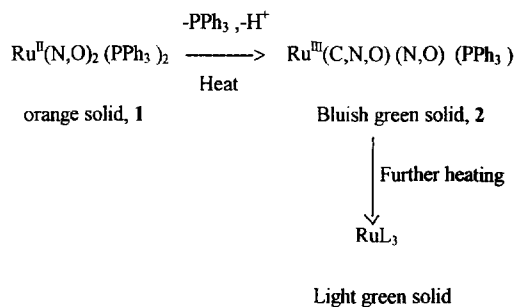
2.8. Rate of conversion of complex **1** to complex **2**

Complex **1** is unstable in solution. It undergoes spontaneous internal conversion to complex **2** in chloroform, dichloromethane and in benzene solutions. The rate of conversion (**1** to **2**) is followed spectrophotometrically in chloroform solvent (Fig. 5). The reaction is first order with respect to **1**. Variable-temperature rate constants (k) and activation parameters are listed in Table 1.

In the presence of 10 times excess phosphines the rate of conversion (**1** to **2**) is found to be reduced (k , s^{-1} ; 0.7×10^{-3} , at 301 K) appreciably. This effect of

Table 1
Rate constants and activation parameters in chloroform solution

Compound	Temperature (K)	k (s^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ ($\text{J K}^{-1} \text{mol}^{-1}$)
1	301	1.33×10^{-3}	10.3	−265
	311	3.16×10^{-3}		
	321	8.16×10^{-3}		



Scheme 2.

external phosphine on the rate of the transformation suggests the involvement of Ru–PPh₃ bond breaking in the slow step. The low $\Delta H^\ddagger$ (~ 10 kJ) value implies that the conversion process (1 to 2) is primarily enthalpy controlled [46]. The observed high negative entropy value (-265 J) is not clearly understood, however, the simultaneously operating processes, ruthenium–phosphorus bond cleavage, formation of new ruthenium–carbon σ bond and oxidation of the metal ion, may account for the observed kinetic behavior.

2.9. Solid state reactivity

In the solid state the complex 1 is perfectly stable at room temperature but upon heating the orange color of the complex 1 is changed to a dark green solid (Scheme 2). Extraction of the dark green solid in chloroform followed by chromatographic purification on an alumina column using chloroform as eluent results in a pure bluish green solution, corresponding to complex 2. The spectroscopic and electrochemical behavior of this bluish green complex are identical to those of the bluish green compound obtained either from the initial reaction (Scheme 1) or through the internal conversion of the orange complex 1 in chloroform solution.

Further heating of the above dark bluish green solid (obtained by any of the above routes) leads to the formation of a new light green solid (Scheme 2). Preliminary studies indicate the correspondence of the light green solid to the RuL₃ complex.

The electron-impact mass spectroscopic studies of the complexes 1 and 2 display identical mass spectra (Fig. 6). In both cases the maximum molecular peak is observed at m/z 732.1, which corresponds to the mass of RuL₃ complex instead of the m/z values of 1 and 2. Thus the heating of either complex 1 or 2 in the solid state leads to the formation of RuL₃ as a final product. The formation of RuL₃ complex from the complex 2 presumably takes place via internal rearrangement.

All attempts to make RuL₃ complex independently from common ruthenium starting materials, RuCl₃, 3H₂O and Ru(DMSO)₄Cl₂ have failed. However, the reaction of Ru(acac)₃ with the ligand HL in ethyl benzoate solvent results in the same greenish RuL₃ complex in impure form which appears to be difficult to purify.

Thermogravimetric analysis (TGA) of the complex 1 shows two-step decomposition. The first decomposition step takes place near 200 °C corresponding to the weight loss of one mole of phosphine leading to the formation of complex 2, and the second decomposition occurs near 283 °C. The isolated complex 2 displays one-step decomposition near 283 °C. The weight loss due to the decomposition at 283 °C is not clearly understood at present.

Further investigations, particularly into the thermal behavior of the complexes and the complete characterization of the RuL₃ species, are in progress.

The internal conversion of the complex 1 to complex 2 is associated with the three primary steps (i) liberation of one PPh₃ ligand from the starting complex, (ii) formation of new ruthenium–carbon σ bond from the hanging phenyl ring of one of the ligands (L) and (iii)

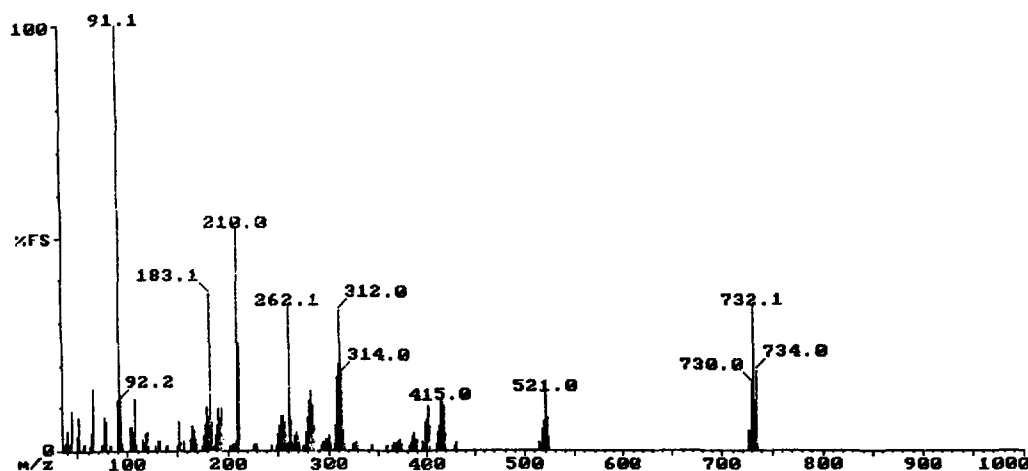


Fig. 6. Mass spectrum of 1.

oxidation of the bivalent ruthenium(II) in **1** to the trivalent ruthenium(III) in **2**.

Since the conversion of **1** to **2** does not proceed through any tractable intermediate, it is therefore difficult to predict the intermediates involved. However, we believe that the release of one PPh_3 molecule from the complex **1** allows the pendant phenyl ring of one of the ligands (L) to come in close proximity to the metal ion. The presence of one CH_2 group between the coordinated imine nitrogen and the pendant phenyl ring of the ligand L facilitates the formation of a new five-membered metallacyclic ring which is, on the other hand, a thermodynamically stable system.

The low ruthenium(III)–ruthenium(II) reduction potential for the complex **2** (-0.68 V) implies that the bivalent Ru(II) congener of the complex **2** may be formed initially as a transient intermediate during the conversion process ($1 \rightarrow 2$) which is then spontaneously oxidized to the trivalent complex **2** under atmospheric conditions.

All our attempts to make suitable single crystals for X-ray characterization of the complex **2** have failed.

Elemental analysis and all other physical data are in agreement with the gross formulation of **2**. Strong support in favor of the presence of metallacyclic ring in the complex **2** is provided by the existence of cyclometallation from the pendant phenyl ring of azobenzene [32], azobenzene thioether [33], azophenol [31] and phenolic Schiff base [34] ligands in the ruthenium complexes.

The complex **2** is highly stable in solution but its conversion to RuL_3 species at high temperature in the solid state is not clearly understood at present. All these are under progress.

3. Conclusion

We have observed ruthenium mediated selective activation of the *ortho* C–H bond of the pendant phenyl ring of L which in turn results in the stable cyclometallated complex **2**. The presence of the methylene (CH_2) group in the amine fragment helps in the formation of cyclometallated complex **2** by providing a minimum requirement to form the thermodynamically stable five-membered metallacycle. The presence of phenolato oxygen in combination with the Ru–C σ -bond in the complex **2** certainly plays an important role in stabilizing the ruthenium ion in the paramagnetic trivalent state.

4. Experimental details

Commercial ruthenium trichloride received from S.D. Fine Chemicals, Bombay, India was purified by repeated evaporation to dryness with concentrated hydro-

chloric acid [47]. The complexes $[\text{Ru}(\text{PPh}_3)_3\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) were prepared according to the reported procedure [48]. The ligand HL was prepared by condensing salicylaldehyde with benzylamine at 273 K. Other chemicals and solvents were reagent grade and used as received. Alumina (neutral) used for chromatography was of BDH quality. For spectroscopic and electrochemical studies HPLC grade acetonitrile, chloroform and dichloromethane solvents were used. Commercial tetraethylammonium bromide was converted into pure tetraethyl ammonium perchlorate by following an available procedure [49].

Solution electrical conductivity was checked using a systronic 305 digital conductivity-bridge. Electronic spectra (900–200 nm) were recorded using a Shimadzu UV-2100 spectrophotometer fitted with a thermostated cell compartment. Near-IR spectra were recorded by using a Hitachi 330 spectrophotometer. Infrared ($4000\text{--}200\text{ cm}^{-1}$) spectra were taken on a Perkin–Elmer 783 spectrophotometer. The magnetic susceptibility was measured on a PAR 155 vibrating-sample magnetometer fitted with a Walker scientific L75FBAL magnet. Electrochemical measurements were done by using a PAR model 362 scanning-potentiostat electrochemistry system. A platinum wire working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel electrode were used in a three-electrode configuration. The supporting electrolyte was NEt_4ClO_4 . The coulometric experiments were done with a PAR model 370-4 electrochemistry apparatus incorporating a 179 digital coulometer. A platinum wire gauze working electrode was used in coulometric experiments.

All electrochemical experiments were carried out under nitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. The EPR measurements were made with a Varian model 109 C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen). The spectrum was calibrated by using tetracyanoethylene (TCNE) ($g = 2.0037$). NMR spectra were obtained with a 300 MHz Varian FT-NMR spectrometer. TGA experiments were performed by using a Dupont 9900 machine. The mass spectra were obtained from an HP 5890 mass spectrometer operating at an electron energy of 70 eV. Microanalyses (C,H,N) were done by using a Perkin–Elmer 240 C elemental analyser.

4.1. Treatment of EPR data

An outline of the procedure can be found in our recent publications [33–38]. We note that a second solution also exists that is different from the chosen one, having small distortions and ν_1, ν_2 values. The experimentally observed near-IR results clearly eliminate the solution as unacceptable.

4.2. Kinetic measurements

The conversion of **1** → **2** was monitored spectrophotometrically in thermostated cells. For the determination of k , the increase in absorption (A_t) at 658 nm was recorded as a function of time t . A_∞ was measured when the intensity changes levelled off. Values of first order rate constants k were obtained from the slopes of linear least-squares plots of $-\ln(A_\infty - A_t)$ against t . A minimum of 30 A_t - t data points were used for each calculation. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained from the Eyring plot [46].

4.3. Synthesis

Complexes **1** and **2** were made by the procedures given below.

4.3.1. Bis-[*N*-benzyl(salicylideneimine)]bis-(triphenylphosphine)ruthenium(II) (**1**) and [*N*-benzyl(salicylideneimine(*N,O*),*N*-benzyl(salicylideneimine(*C,N,O*)]-(triphenylphosphine)ruthenium(III) (**2**)

A suspension of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (0.10 g, 0.10 mmol) in 20 cm³ of ethanol was refluxed for 2 min, and the ligand HL (0.04 g, 0.20 mmol) was then added. The mixture was heated under reflux for 4 h and then allowed to cool. An orange solid and deep green solution were formed. The orange crystalline solid complex **1** separated was filtered off and washed thoroughly with ethanol and diethylether and then dried in vacuum over P_4O_{10} . Yield 40%. Anal. Found: C, 73.28; H, 4.96; N, 2.63. **1** Calc.: C, 73.49; H, 5.16; N, 2.68%.

On removal of the solvent from the green filtrate a green solid mass (complex **2**) was obtained. It was then dissolved in a small volume of chloroform and purified by using an alumina (neutral) column. With benzene (as eluent) a slight amount of light yellow solution due to the excess ligand was separated first and rejected. Using chloroform as eluent a deep bluish green band was eluted. It was collected and evaporation of the solvent under reduced pressure afforded a crystalline solid. Yield 50%. Anal. Found: C, 70.49; H, 4.80; N, 3.45. **2** Calc.: C, 70.58; H, 4.86; N, 3.58%.

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