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Synthesis, characterisation and reactivity of *trans*-[Ru(L)(PPh₃)Br₂]; L=2pyridyl-*N*-(2'-methylthiophenyl)methyleneimine Crystal structure of *trans*-[Ru(L)(PPh₃)Br₂]

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Abstract

Reaction of $Ru(PPh_3)_2Br_2$ with the NNS chelating tridentate ligand 2-pyridyl-*N*-(2'-methylthiophenyl)methyleneimine (L) led to the isolation of the ruthenium(II) complex [$Ru(L)(PPh_3)Br_2$]. Reactivity of this complex with different bidentate chelating ligands revealed that the products are quite different from those obtained by reacting $Ru(L)(PPh_3)Cl_2$ (the corresponding *cis* dichloro complex) with the same ligands under comparable conditions. The mixed chelates were isolated and characterised by elemental analysis, magnetic moment measurement and by different spectroscopic methods along with their precursor. Electrochemistry of the complexes was examined by cyclic voltammetry using a platinum working electrode and a Ag/AgCl electrode as reference. The crystal structure of [$Ru(L)(PPh_3)Br_2$] disclosed that, unlike $Ru(L)(PPh_3)Cl_2$, the two bromo ligands are in *trans* position and this explained the difference in its reactivity pattern from the corresponding chloro complex. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ruthenium(II) complexes; Trans dibromo complex; NNS ligand; Chemical and electrochemical studies; X-ray crystal structure

1. Introduction

In our exploration of the chemistry of ruthenium coordinated to different types [1-11] of mixed hard-soft N–S chelating ligands, we reported the synthesis, crystal structure and reactivity of *cis*-Ru(L)(PPh₃)Cl₂ (A) [L=2-pyridyl-*N*-(2'-methylthiophenyl)methyleneimine] in a recent publication [11]. In this work (A) was prepared by reacting Ru(PPh₃)₃Cl₂ with the ligand (L) in refluxing benzene. When we reacted Ru(PPh₃)₃Br₂ with the ligand under identical conditions, a product of similar composition, Ru(L)(PPh₃)Br₂ (1), was obtained. However, the reactivity pattern of (1) was found to be quite different from that of (A) with respect to similar reagents under identical experimental conditions. Metathetical reactions of (1) with bidentate ligands lead to the formation of a number of compounds having compositions quite different

from those of the corresponding complexes obtained from (A) and none of the resultant species contain any triphenylphosphine though its precursor is Ru(L)(PPh₃)Br₂ Each of the complexes prepared from (A), however, contains one triphenylphosphine moiety. It is difficult to explain such observations because the Ru-Br bond is weaker than the Ru-Cl bond. Also, if complex (1) is structurally similar to (A), it is expected to yield similar types of mixed chelates. In order to find an unambiguous solution to this problem we prepared good single crystals of (1) and determined their structure by X-ray diffraction. It was then confirmed that (1) is $trans-Ru(L)(PPh_3)Br_2$. This finding explained the difference in the reactivity pattern of (A) and (1). The difference between the stereochemistry of (A) and (1) may be due to steric factors and/or the electronic character of the monodentate ligands attached to the Ru(II) centre since the size of the ligands increase in the order of Cl<Br<PPh3. The steric factor alone could not preclude the formation of the cis-dibromo derivative. However, in practice we find that instead of two bromo ligands, one PPh₃ and one bromo ligands occupy

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cis positions in (1). This observation points to the fact that the electronic factor is also playing an important role in deciding the actual stereochemistry of the compounds (A) and (1). The importance of the electronic factor is also evidenced from the fact that the presence of the triphenylphosphine moiety raise the Ru(II)/Ru(III) oxidation potential compared to those having no triphenylphosphine moiety.

2. Experimental

 $RuCl_3$ was purchased from Arora-Matthey Limited. $Ru(PPh_3)_3Cl_2$ [12] was prepared using a previously published procedure. The ligand 2-pyridyl-*N*-(2'-methylthiophenyl)methyleneimine (L) was prepared according to the literature [11]. All other common chemicals and solvents used were of reagent grade and were used as received. Acetonitrile obtained from E. Merck (India), was freshly distilled over CaH₂ prior to electrochemical experiments.

2.1. Physical measurements

Elemental analyses were performed on a Perkin Elmer 240 CHNS/O analyser. Solution conductance was measured on a Systronics direct reading conductivity meter (model 304), and room temperature magnetic moments were measured with a PAR vibrating sample magnetometer using Hg[Co(SCN)₄] as calibrant. IR and electronic spectra were recorded on a Perkin Elmer 783 IR spectrophotometer and Shimadzu UV–Vis recording spectrophotometer, respectively. NMR spectra were recorded on a Bruker 300-MHz NMR spectrometer using TMS as the internal standard. Cyclic voltammetry experiments were carried out on a BioAnalytical System (BAS) 27 electrochemical analyser and a BAS Model X–Y recorder using a platinum disc electrode.

2.2. Preparation of the complexes

2.2.1. Trans- $Ru(L)(PPh_3)Br_2$ (1)

First, 1049 mg (1 mmol) of Ru(PPh₃)₃Br₂ was dissolved in 40 ml benzene and the solid ligand (470 mg, 2 mmol) was added to it followed by 30 ml of benzene. The mixture was refluxed for 5 h. The compound separated out within 30 min. The reaction mixture was cooled and filtered. The dark violet residue was washed thoroughly with benzene and dried in vacuo over fused CaCl₂. Yield: 600 mg, 80%. Anal. found: C, 49.7; H, 3.4; N, 3.9. Calcd. for RuC₃₁H₂₇N₂SPBr₂: C, 49.5; H, 3.6, N, 3.7%. Conductance in CH₃CN ($\Lambda_{\rm M}$) 40 Ohm⁻¹ cm² mol⁻¹.

2.2.2. $[Ru(L)(en) Br](PF_6)$ (2)

First, 375 mg (0.5 mmol) of compound 1 and 30 mg (0.5 mmol) of ethylenediamine was dissolved in 50 ml of

methanol and the mixture was refluxed for about 12 h. After cooling, the volume was reduced to one-third of its original volume in a rotary evaporator and the compound precipitated with aqueous ammonium hexafluorophosphate solution. The precipitate was filtered and washed throughly with water. The compound was dried over fused CaCl₂ and recrystallised from MeOH/EtOH. Yield: 230 mg, 75%. Anal. found: C, 29.2; H, 3.3; N, 9.0. Calcd. for RuC₃₁H₂₇N₂SPBr₂: C, 29.3; H, 3.2, N, 9.1%. Conductance in CH₃CN ($\Lambda_{\rm M}$) 132 Ohm⁻¹ cm² mol⁻¹.

2.2.3. [Ru(L)(pic)Br] (3)

Again, 375 mg (0.5 mmol) of compound **1** was dissolved in 50 ml of methanol. Then, 70 mg (0.5 mmol) of picolinic acid and 0.60 mg (0.5 mmol) of sodium carbonate was added and the mixture was refluxed for 12 h. After cooling, the volume of the solution was reduced in a rotary evaporator. The compound was then precipitated with ether, filtered and washed with ether. The compound was dried over fused CaCl₂ and recrystalised from MeOH/ Et₂O. Yield: 186 mg, 70%. Anal. found: C,.43.0; H, 3.0; N, 7.8. Calcd. for RuC₃₁H₂₇N₂SPBr₂: C, 42.9; H, 3.0, N, 7.9%. Conductance in CH₃CN ($\Lambda_{\rm M}$) 30 Ohm⁻¹ cm² mol⁻¹.

2.2.4. [Ru(L)(ox)Br] (4)

First, 375 mg (0.5 mmol) of compound **1** was dissolved in 50 ml of methanol, then 80 mg (0.5 mmol) of oxine and 60 mg (0.5 mmol) of sodium carbonate was added and the mixture refluxed for 12 h. After cooling, the volume of the solution was reduced in a rotary evaporator. The compound was precipitated with ether. It was then filtered, washed with ether, dried over fused CaCl₂ and recrystallised from MeOH/Et₂O. Yield: 199 mg, 72%. Anal. found: C, 47.5; H, 3.3; N, 7.5. Calcd. for RuC₃₁H₂₇N₂SPBr₂: C, 47.6; H, 3.2, N, 7.6%. Conductance in CH₃CN ($\Lambda_{\rm M}$) 37 Ohm⁻¹ cm² mol⁻¹.

2.3. Crystallographic structure determinations

A single crystal of the complex $Ru(L)(PPh_3)Br_2$ suitable for X-ray structure determination was grown by slow diffusion of petroleum ether into a dichloromethane solution of the compound. A deep brown crystal of dimension $0.25 \times 0.13 \times 1.2$ mm was used for data collection. Accurate unit cell parameters were determined by a least-square fit of 25 machine-centered reflections in the range $24 < 2\theta <$ 36°. Data were collected at 293 K on a PC-controlled Nonius CAD-4 single crystal X-ray diffractometer using Mo K α radiation (λ =0.7107 Å). Three standard reflections measured every hour showed <4% variation in average intensity. The structure was solved using MULTAN-80 (NRCVAX programs) [13]. Full matrix least-squares refinement on F^2 of scale factor and positional anisotropic thermal parameters for non-hydrogen atoms using SHELXL-93 [14] converged to a final R = 0.073 and and Rw = 0.219



Fig. 1. ORTEP diagram and atom numbering scheme of $trans-Ru(L)(PPh_3)Br_2$ (1).

(using reflections with $I \ge 2\sigma(I)$ only). One molecule of dichloromethane was located from the difference Fourier. It was found to be disordered, with each chlorine atom occupying two different positions of equal occupancy. The solvent atoms were refined isotropically (Fig. 1). Coordinates of the hydrogen atoms (except the one for solvent molecule) were geometrically determined and held fixed during the refinement. The hydrogen atom scattering contribution was included in the subsequent calculations. The crystal data, data collection and refinement parameters are summarised in Table 1.

3. Results and discussion

3.1. Description of the crystal structure of compound 1

Compound 1 has a similar composition to the corre-

Table 1 Crystallographic data for *trans*-[Ru(L)(PPh₃)Br₂] (1)

Formula	$C_{31}H_{27}Br_2N_2PRuS \cdot CH_2Cl_2$
Formula weight	835.38
Crystal system	Triclinic
Space group	PĪ
a (Å)	10.651(2)
b (Å)	12.065(2)
<i>c</i> (Å)	14.918(2)
α (°)	113.53(2)
β (°)	89.78(2)
γ (°)	103.23(2)
$V(\text{\AA}^3)$	1702.7(5)
Z	2
λ (Å)	0.70930
$\rho_{\rm calc} \ ({\rm g \ cm}^{-3})$	1.629
$\mu (\mathrm{mm}^{-1})$	3.097
R(F)	0.0730
wR(F)	0.2189
$GOF(F^2)$	1.027

sponding chloro compound but they differ in stereochemistry, i.e. disposition of the donor atoms around the ruthenium centre. In bromo compound 1, two bromo ligands are trans but in chloro compound (A) the two chloro ligands are cis to each other. The coordination geometry around ruthenium is distorted octahedral. The ligand acts as a tridentate donor coordinating to the ruthenium(II) center through pyridine nitrogen N(1), imine nitrogen N(2), and thioether sulfur(S), which occupy three positions of the equatorial plane; the forth position being occupied by a triphenylphosphine moiety. The two axial positions are occupied by two bromo ligands. The Ru-S bond length of the complex 1 (2.314 Å) is nearly equal to the corresponding bond length (2.309 Å) of the chloro complex (Table 2). The rather short distance of this bond [15] indicates a strong ruthenium thioether interaction. The Ru–P distance in the bromo complex (2.341 Å) is larger than that of the chloro (2.292 Å) complex. In the bromo complex there is a competition of π -back bonding between PPh₃ and imine nitrogen but in the chloro complex such π -bonding of the chloro ligand trans to PPh₃ is not so effective. This phenomenon is reflected in the slightly longer Ru–N(2) imine (2.034 Å) bond distance in the bromo complex compared to that of the Ru-N(9) (1.988 Å) distance in the chloro complex.

All compounds are diamagnetic at room temperature. Compounds 1, 3, and 4 are non-electrolytes and compound 2 behaves as a 1:1 electrolyte in acetonitrile. The ligand (L) behaves as a neutral tridentate ligand. The involvement of the pyridine nitrogen, imine nitrogen and thioether sulfur of the ligand in coordination to the ruthenium centre is indicated by analysis of IR spectra (Table 3). The pyridine ring vibrations at 630 and 430 cm⁻¹, a fairly strong band at 1620 cm⁻¹, assigned to ν (CN) vibration and the ν (CS) band present at 790 and 760 cm⁻¹ in the free ligand are found to undergo a red shift in the

Table 2 Selected bond lengths (Å) and bond angles (°) for *trans*-IRn(L)(PPh)Br(L)

$[Ku(L)(PPII_3)DI_2]$	(1)		
Ru–Br(1)	2.502(2)	Ru–Br(2)	2.531(2)
Ru-N(2)	2.034(8)	Ru-N(1)	2.089(8)
Ru–S	2.314(3)	Ru–P	2.341(3)
C(13)–S	1.814(11)	C(12)–S	1.789(11)
C(7)–C(12)	1.41(2)	C(6)–N(2)	1.276(14)
C(5) - C(6)	1.45(2)	C(5) - N(1)	1.340(13)
P-C(14)	1.848(11)	P-C(27)	1.823(10)
P-C(26)	1.841(11)		
N(1)-Ru-N(2)	78.6(3)	N(2)-Ru-S	84.2(3)
N(1)-Ru-S	162.8(2)	N(2)-Ru-P	177.2(3)
N(1)-Ru-P	100.6(2)	S-Ru-P	96.59(10)
N(2)-Ru-Br(1)	84.3(2)	N(1)-Ru-Br(1)	84.7(2)
S-Ru-Br(1)	94.11(8)	Br(1)-Ru-P	98.29(8)
N(2)-Ru-Br(2)	87.9(2)	N(1)-Ru-Br(2)	95.0(2)
S-Ru-Br(2)	83.81(8)	Br(2)-Ru-P	89.57(8)
Br(1)-Ru-Br(2)	172.06(6)	C(12)-S-C(13)	100.9(6)
C(12)-S-Ru	98.5(4)	C(13)-S-Ru	114.3(4)

Table 3									
Important	IR	bands	(in	cm^{-1}) of	the	com	plexes	

Compound	$\nu(\mathrm{NH}_2)$	ν (C=C)+ ν (C=N)	$\nu(CS)$	Other frequencies
L		1620, 1580, 1570, 1510	790, 760	630, 580, 490, 420
$[Ru(L)(PPh_3)Br_2] (1)$		1620 (sh) ^a , 1590, 1515	775, 750	620, 570, 480, 420
$[Ru(L)(en)Br]PF_{6}$ (2)	3320, 3220	1645, 1595, 1575,	770, 740	850, 550, 520, 460, 420
[Ru(L)(pic)Br] (3)		1640, 1595, 1575, 1555	770, 745	695, 520, 445, 420
[Ru(L)(oxin)Br] (4)		1605, 1580, 1550	775, 745	690, 570, 505, 455, 420

^a sh, shoulder.

complexes due to M–N and M–S bond formation [16,17]. The strong, broad band at 850 cm⁻¹ indicates the presence of ionic hexafluorophosphate in compound **2**. The broad band centered at 1690 cm⁻¹ due to the presence of free carboxylic acid group of picolinic acid is lowered to 1605^{-1} on complexation. The presence of the NH₂ proton of ethylenediamine in complex **2** is revealed by the symmetric and assymmetric ν (N–H) modes at 3320 and 3220 cm⁻¹ and the NH₂ bending at 1645 cm⁻¹.

3.2. Electrochemistry

The redox behaviour of the complexes were studied by cyclic voltammetry in acetonitrile (Table 4). All the compounds show one Ru(II)/Ru(III) oxidation on the positive side. The separation between the anodic and the cathodic peak (ΔE_p) value is close to the ideal Nernstian value of 59 mV and $i_{pc}/i_{pa} = 1$. So the Ru(II)/Ru(III) couple is reversible. The $E_{Ru(II)/Ru(III)}^{\circ}$ value of the bromo complex is lower than that of the chloro complex indicates that chloro ligands stabilize the Ru(II) state more than the

Table 4

Cyclic voltammetric results^{a,b} of the complexes in CH₃CN

Complex	$E_{1/2}/V(\Delta E_{\rm p},{\rm mV})$ Oxidation
$[Ru(L)(PPh_3)Br_2] (1)$	0.39(60)
$[\operatorname{Ru}(L)(\operatorname{en})\operatorname{Br}]\operatorname{PF}_{6}(2)$	0.59(60)
[Ru(L)(pic)Br] (3)	0.22(60)
$[\operatorname{Ru}(L)(\operatorname{oxin})\operatorname{Br}]$ (4)	0.42(60)

^a Working electrode, glassy carbon; reference electrode, Ag/AgCl; $E_{1/2} = 0.5 (E_{pc} + E_{pa})$, where E_{pc} and E_{pa} are cathodic and anodic peak potentials, respectively. Supporting electrolyte 0.1 M TEAP; solute concentration 10^{-3} M; scan rate 50 mV s⁻¹.

^b Peak height of the couple compared with one-electron oxidation of Ru(II)/Ru(III) of *cis*-[Ru(bpy)₂Cl₂] under identical molar concentration and experimental conditions.

Table 5 Electronic spectral data of the complexes in CH CN

bromo ligands. This effect may be due to the higher electronegativity of the chlorine atom [6,7]. Reactions of $[Ru(L)(PPh_3)Br_2]$ with a different bidentate ligand (L')gives compounds of the general formula $[Ru(L)(L')Br]^{0/4}$ formed by the substitution of a PPh3 and a Br ligand. All these compounds exhibit a lower $E^{\circ}_{Ru(II)/Ru(III)}$ potential than that of the mother compound, which indicates that all the three bidentate ligands are less effective in stabilising the Ru(II) oxidation state compared to PPh₃ and Br jointly. Among the three complexes, monocation compound 2 shows a higher $E^{\circ}_{Ru(II)/Ru(III)}$ potential than that of the neutral compounds [18,19]. Though both picolinic acid and oxine are uninegative donors, the oxinate compound is more difficult to oxidise than that of the picolinate compound due to greater delocalisation of the $d\pi$ electrons in the oxinate complex than in the picolinate complex, because oxine has more low lying π^* orbital to receive back donated electron from the Ru(II) centre and stabilise the Ru(II) state.

3.3. Electronic spectra

The electronic spectra of Ru(II) complexes is dominated by charge transfer transitions (Table 5). In the free ligands there are three bands at 380, 251 and 210 nm. The bands at 251 and 210 nm can be interpreted as $\pi \rightarrow \pi^*$ transitions of the pyridine and phenyl ring respectively, the band at 380 nm is probably a charge transfer transition from the filled sulfur orbital to one of the π^* orbital of the diimine moiety. In the asymmetric crystal field prevailing in the complexes, the $d\pi$ orbitals of Ru(II) are expected to be non degenerate. Considering the number of vacant π^* orbitals of suitable symmetry in the thioether ligand as well as in the coligands, a large number of metal-to-ligand charge transfer transitions are expected, in addition to the intraligand charge transfer transitions. This makes the

Electronic spectral data of the complexes in CH3ert	
Complex	$\lambda_{\rm max}/{\rm nm}~(\epsilon \times 10^{-3},~{\rm M}^{-1}~{\rm cm}^{-1})$
$[\operatorname{Ru}(L)(\operatorname{PPh}_3)\operatorname{Br}_2](1)$	282(4.3), 314(0.664), 338(0.463), 516(0.142), 596(0.0157)
$[\operatorname{Ru}(L)(\operatorname{en})\operatorname{Br}]\operatorname{PF}_6(2)$	226(1.906), 307(0.6515), 341 (sh) ^a (0.4228), 365 (sh) ^a (0.2876), 490(0.1525)
[Ru(L)(pic)Br] (3)	227(2.3112), 307(0.8985), 341 (sh) ^a (0.6847), 359 (sh) ^a (0.4599), 518(0.1907)
[Ru(L)(oxin)Br] (4)	227(1.9728), 250(1.3929), 315(0.3717), 357 (sh) ^a (0.2710), 406(0.3008), 468 (sh) ^a (0.2103)

^a sh, shoulder.

interpretation of the electronic spectra extremely difficult. However, it may be concluded that bands in the 400–600 nm region are due to MLCT involving $\operatorname{Ru}(d\pi) \rightarrow S(d\pi)$ and $\operatorname{Ru}(d\pi) \rightarrow \pi^*$ (imine) transitions. Besides, in some of the complexes there is an additional MLCT band around 360 nm. The two bands around 340 and 310 nm are probably intraligand charge transfer transitions, while the band below 300 nm are due to $\pi \rightarrow \pi^*$ transitions of pyridine and phenyl rings.

3.4. NMR spectra

The methyl signal of the free ligand is observed at 2.37 ppm [20]. On complexation, this signal appears at different δ values for different complexes, ranging from δ 1.25 to 2.1 ppm. The two CH₂ signals of the ethylenediamine complex appear at 2.95 and 2.88 ppm. The phenyl protons are observed in the δ 6.0–7.3 range.

4. Conclusion

This study points to the fact that a particular procedure involving similar reactants can lead to chemically and structurally different products. When the ligand 2-pyridyl-N-(2'-methylthiophenyl) methyleneimine reacts with the very similar Ru(II) complexes $Ru(PPh_3)_3Cl_2$ and $Ru(PPh_3)_3Br_2$, two different complexes of the same general formula $Ru(L)(PPh_3)X_2$ (X = Cl/Br) were isolated. But the reactivity pattern of the two are found to be entirely different. Structure determination of (A) showed that it is a *cis* dichloro derivative and all its metathetical reactions with chelating bidentate ligands lead to the displacement of the two cis-dichloro groups. However, the reactions of (1) with the same ligand lead to the formation of mixed chelates with the displacement of one Br and the PPh₃ moiety instead of the two Br ligands. This difference in reactivity points to structural dissimilarity between (A) and (1). X-ray analysis of a single crystal of (1) showed that the two Br groups are trans to each other and the replacement of one Br and the PPh₃ instead of the two Br groups (as is observed in $Ru(L)(PPh_3)Cl_2$) could be explained.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 132815.

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