ISOMERIC COMPLEXES OF RUTHENIUM(II) WITH NEUTRAL HETEROCYCLIC SCHIFF BASE LIGANDS. HIGH RESOLUTION PROTON RESONANCE SPECTRA OF TRANS-CIS ISOMERIC PAIRS OF RuX₂L₂ (L = 2-ARYLPYRIDINECARBOXALDIMINE, X = Cl, Br) AND COMPARISON OF THEIR PHYSICAL PROPERTIES

SUBRATA CHOUDHURY, MAUSHUMI KAKOTI, ALOK K. DEB[†] and SREEBRATA GOSWAMI[‡]

Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India

(Received 11 June 1992; accepted 3 August 1992)

Abstract—The reaction of 2-arylpyridinecarboxaldimine [RH₄C₆NC(H)Py, L (1)] with hydrated RuX₃ (X = Cl, Br) in boiling C₂H₅OH affords dark crystals of RuX₂L₂. Two geometrical isomers of the compound have been isolated and characterized by analytical and spectroscopic data. The *trans* isomer of RuCl₂L₂ shows a single sharp band for v(Ru—Cl), whereas two bands are observed for the corresponding *cis* isomer. The highresolution ¹H NMR spectra of the isolated complexes are reported and completely assigned. All the complexes have multiple $t_2 \rightarrow \pi^*(L)$ transitions in the visible region. Each of the complexes display a quasi-reversible oxidative response due to an Ru^{III}/Ru^{II} couple in the range 0.25–0.40 V vs S.C.E. at a platinum working electrode. The formal potentials of this couple obey the Hammett relationship. The ligand-based irreversible oxidations are also briefly noted.

The chemistry of ruthenium complexes of unsaturated nitrogenous ligands is quite extensive.^{1,2} However, the Schiff base complexes of ruthenium in general, and bivalent ruthenium in particular, represent³⁻⁹ a relatively unexplored area of chemistry. Our interest in platinum group metal complexes^{10,11} with organic ligands with varying degrees of σ basicity and π -acidity led us to explore the ruthenium chemistry of a neutral Schiff base ligand system, 2-arylpyridinecarboxaldimine [L (1)]. The ligand L has an α, α' -diimine fragment and it may be noted that most of the α, α' -diimine complexes of ruthenium(II) generally show charge-transfer emission—a property that can help in mediating^{12–14} important photo-induced reactions.

In recent years only a few reports¹⁵⁻¹⁷ of ruthenium complexes of L or related ligands have appeared. In the present report we describe the successful synthesis and characterization of isomeric

bischelated ruthenium(II) complexes of the general type RuX_2L_2 (X = Cl, Br). Stereochemical assessments of the complexes are made on the basis of their spectral data.

RESULTS AND DISCUSSION

Synthesis and formulation

Three ligands (1a–1c), differing with respect to substituents on the aryl ring, were used for the present work. The ligands were generally obtained by the condensation of pyridine-2-carboxaldehyde and the appropriate primary aromatic amine, in a 1:1 ratio in absolute C_2H_5OH . The ligands were generated¹⁷ in situ and used directly for the syntheses of ruthenium complexes. The reactions of hydrated RuCl₃ with L in the presence of excess LiX (X = Cl, Br) proceeded smoothly in refluxing C_2H_5OH to yield a mixture of compounds containing two major fractions, each of which had the formula RuX₂L₂. One (green) was sparingly soluble in ethanol and deposited in the reaction vessel on

[†] Present address : Department of Chemistry, Shillong Polytechnic, Shillong 8, India.

[‡] Author to whom correspondence should be addressed.

		Serial number		
L	Х	green, trans	bluish-green, cis	
1a	Cl	2a	3a	
1a	Br	4a	5a	
1b	Cl	2b	3b	
1b	Br	4b	5b	
1c	Cl	2c	3c	

Table 1. Serial numbers of RuX_2L_2

cooling. The second component (bluish-green) was isolated from the violet filtrate on chromatographic work-up. This was done on a silica gel column using different mixtures of CHCl₃ and CH₃CN (see the Experimental) as the eluant. Yields of RuX_2L_2 varied from 50 to 55%. The dihalo complexes examined in the present work are numbered as shown in Table 1. To date we have not isolated a tris-complex from the above reaction. It may be relevant to add here that the reaction of $RuCl_3$ with preformed¹⁷ **1b** also afforded a similar mixture of $\operatorname{RuCl}_2(L^2)_2$ without improvement of the yield. The compounds were formulated¹⁸ by elemental analyses and are diamagnetic, more soluble in less polar solvents such as CHCl₃ and CH₂Cl₂ and are non-electrolytic in CH₃CN.

Spectra and assessment of structure

IR spectra. IR spectral data were collected as KBr discs in the range 4000–250 cm⁻¹. Selected group frequencies are presented in Table 2. All of the complexes show the characteristic absorptions for coordinated L in their IR spectra. In free L

v(C=N) is observed at ca 1625 cm⁻¹. This frequency is lowered in the complexes, $^{19} ca 1600 \text{ cm}^{-1}$. The assignment of v(Ru-X) is made by comparison of the IR spectrum of $RuCl_2L_2$ with those of $RuBr_2L_2$ and free L in the range 400–250 cm⁻¹. The free ligand, L, does not show any absorptions below 350 cm^{-1} . All the dichloro complexes exhibit a moderately strong band(s) at $ca 300 \text{ cm}^{-1}$, which is conspicuously absent in $RuBr_2L_2$. Evidently, this band in the IR spectrum of $RuCl_2L_2$ is due²⁰ to the v(Ru—Cl) stretching mode. We could not identify v(Ru - Br) which probably lies²⁰ below our experimentally accessible range. Interestingly, the Ru-Cl stretching mode in the green isomer of $RuCl_2L_2$ appears as a single band, whereas that in the bluish-green isomer appears as a two-band structure (Table 2). The singlet nature of v(Ru-Cl) strongly suggests²⁰⁻²² a linear *trans* grouping for the RuCl₂ moiety and the doublet v(Ru-Cl) is expected^{11,21,22} for a *cis*-RuCl₂ grouping. Thus, from the IR data we conclude that the green isomer is trans with respect to two Cls and the other isomer has a *cis*-RuCl₂ geometry. The dibromo analogue has a virtually identical IR spectrum in the range 4000-350 cm⁻¹, indicating that the gross geometries of the two isomers of $RuBr_2L_2$ are similar to those of RuCl₂L₂.

¹H *NMR spectra*. The geometries of the isomeric RuX_2L_2 were mainly assessed by an examination of the high-resolution ¹H NMR spectra of the compounds. Three pairs of isomeric $RuCl_2L_2$ were chosen for this purpose. All of them displayed highly resolved spectra in CDCl₃. Two representative spectra are displayed in Fig. 1 and the data are collected in Table 3. Different protons are numbered as shown in Structure 1. We first consider

Table 2. Optical spectral data for RuX₂L₂

	$IR^{a} v_{max} (cm^{-1}) $ Electronic spectra ^b		
Compound	C=N	Ru—Cl	λ_{\max} (nm) (ϵ , M^{-1} cm ⁻¹)
2a	1605	302	675 (8200), 620 (10,050), 570, ^c 425 (3725), 390, ^c 290 (13,250), 270 (13,325)
3a	1605	310, 295	675 (6100), 605 (10,870), 555, ^c 425 (2680), 345 (10,240), 280 (15,540)
4 a	1610		665 (7360), 618 (10,100), 570,° 425 (3550), 385,° 300 (11,970), 270 (12,925)
5a	1605		665 (5320), 605 (10,820), 560, ^c 420 (2925), 365 (8150), 280 (13,300)
2b ^d	1600	305	675 (6960), 620 (8900), 570, ^c 425 (3340), 390, ^c 310 (10,670), 270 (12,050)
3b	1605	310, 290	675 (5475), 605 (10,020), 560,° 425 (2500), 360 (10,200), 282 (15,210)
4b	1610	-	670 (6100), 618 (10,530), 570,° 425 (3210), 390,° 305 (11,550)
5b	1600		670 (3950), 610 (9300), 560, 435 (3110), 365 (8800), 285 (12,300)
2c	1605	300	680 (7250), 618 (8790), 570, 425 (3370), 375, 310, 280 (14,610)
3c	1600	310, 295	680 (5620), 608 (9500), 560,° 425 (2550), 345 (10,950), 285 (17,370)

^a In KBr discs; bands are of strong or medium intensities.

^b In CHCl₃.

^c Shoulder.

^d Compound 1b shows two absorptions (Fig. 3) at 330 (3240) and 270 nm (5910).



the spectra of the bluish-green isomer. The spectrum of 3a consists of seven aromatic resonances in the range 6.9–9.4 δ . Two doublet and two triplet resonances, each of which corresponds to one proton signal, in the range 7.6–9.4 δ are assigned^{23–26} to pyridyl proton signals (Fig. 1, Table 3). Three more resonances were observed at higher magnetic fields. The signal at 7.20 δ is a doublet and its area corresponds to two protons. This is surely due to coincident doublet signals of 8-H and 12-H. The rest of the two signals are both triplets—the triplet at the higher field is twice the intensity of the other signal. Therefore, we conclude that the resonance at 7.03 δ is for 10-H, whereas the signal at 6.98 δ is due to 9-H and 11-H. In contrast to the seven aromatic resonances for 3a, only six have been observed each for 3b and 3c. In these cases the signal for 10-H is absent and 9-H and 11-H signals



Fig. 1. ¹H NMR spectra of (a) *trans*-RuCl₂(L^1)₂ and (b) *cis*-RuCl₂(L^1)₂ in CDCl₃.

			Table	3. H NMR sp	ectral data for H	RuCl ₂ L ₂ in CDC	1,			
					δ^a (ppm) (J ,	, Hz) ^b				
Compound	H(3)	H(4)	H(5)	H(6)	H(8)	(6)H	H(10)	H(11)	H(12)	H(13)
2a	7.84(7.50)	7.64(7.60) ^d	$6.92(6.68)^{d}$	7.77(5.65) ^c	$7.80(7.60)^{c}$	7.56-7.50	7.56-7.50	7.56-7.50	7.80(7.60) ^c	8.92
3a	7.96(7.40) ^c	$7.90(7.60)^{d}$	$7.59(6.30)^{d}$	$9.37(5.00)^{c}$	$7.20(7.50)^{e}$	$6.90(7.40)^{d}$	$7.03(7.20)^{d}$	$6.90(7.40)^{d}$	$7.20(7.50)^{c}$	8.80
2b	7.83(7.45) ^c	$7.63(7.20)^{d}$	$6.93(6.67)^d$	$7.86(5.60)^{c}$	$7.68(8.15)^{c}$	7.32(8.00)	,	7.32(8.00)	7.68(8.15)	8.90
3b	7.95(7.50) ^c	$7.89(7.50)^{d}$	$7.58(6.20)^{d}$	$9.36(5.30)^{c}$	$7.09(7.70)^{c}$	6.71(7.80)	ſ	$6.71(7.80)^{c}$	7.09(7.70)°	8.78
2c	7.88(7.90) ^c	$7.70(7.60)^{d}$	$7.05(6.60)^{d}$	7.87(5.90) ^c	7.51(8.55) ^c	$7.76(8.40)^{c}$		$7.76(8.40)^{c}$	7.51(8.55) ^e	8.91
સ	7.99(7.60)	7.93(7.60) ^d	$7.63(6.50)^{d}$	9.35(5.50) ^c	7.16(8.50) ^c	6.98(8.40) ^c		6.98(8.40) ^c	7.16(8.50) ^c	8.79°
" Tetrametl	hylsilane is the	internal standa	rd.							
^b Spin-spin ^c Doublet.	coupling amo	ngst nearest neig	ghbour protons (only.						
^d Triplet.										
' Singlet.										

ī

1

I

Me(10) for trans and cis geometries at 2.48 and 2.28 ppm, respectively.



appear as coincident doublets. Each of these complexes (**3a-3c**) displays a sharp singlet at $ca \ 8.8\delta$, assignable to 13-H, and **3b** shows an additional singlet methyl resonance at 2.28 ppm.

The pattern of the spectra of 2 is completely different from that of 3 (Fig. 1). Aromatic resonances for the green isomers were observed in the range $6.8-7.9\delta$. In this range 2b and 2c show six aromatic resonances. Of these, two at 7.32 and 7.68 δ are twice as intense as the other four signals. These two signals are due to coincident doublets arising from two pairs of protons, viz. 9-H, 11-H and 8-H, 12-H, respectively. Compound 2b also shows an additional single and sharp methyl resonance at 2.48 δ . The spectrum of 2a is as expected. Each of the green isomers of RuCl₂L₂ also shows a sharp signal at 8.90 ppm, which is assigned to the 13-H resonance.

It may be noted here that the spectra of both 2 and 3 exhibited one signal for each proton of the ligand L. From these data we conclude that the isolated compounds are isomerically pure and the two chelate rings in both the isomers of RuCl₂L₂ are magnetically equivalent, at least on an NMR time-scale. In principle, five geometrical isomers are possible^{20,21} for the RuX_2L_2 moeity. Of the five possible structures, one cis isomer (ccc) does not contain any symmetry axis and the formation of one of the *trans* isomers, viz. *tcc*, is unlikely due to serious steric crowding²⁰ of the two *cis*-aryl rings. Therefore, the isolated isomers of RuCl₂L₂ could only be two of three possibilities, viz. ttt, ctc and cct. Further examination of the data presented in Table 3 reveals that the pyridyl protons in the green isomer are shielded in general, and the 6-H and 5-H protons in particular, compared to those in the bluish-green isomer. This strongly suggests that the green isomer is the most symmetrical ttt isomer. In this geometry, each of the pyridyl ring protons are in close proximity (structure ttt) to the aryl ring of the second ligand and 6-H would be closest to the aryl ring. Thus, it is expected that 6-H would be



shielded by the aryl ring current and would resonate at a higher field. It is also interesting to note that in the bluish-green isomer the 6-H resonance appears at a much lower field. This result is in accord with the *cis* configuration (with respect to two chlorides), where each 6-H is pointed either at a chloride (ctc) or an imine nitrogen (cct). In these geometries negligible shielding or even deshielding of 6-H would be expected. Therefore, based on the ¹H NMR data we conclude that the geometry of 2 is surely *trans*, ttt, and that of 3 is one of the two cis structures (either *ctc* or *cct*) having a C_2 symmetry axis. This ambiguity about the stereochemistry of the bluishgreen isomer cannot be settled by 'H NMR data. Final verification of the structure in this case requires an X-ray structure determination. Unfortunately, we are yet to isolate suitable crystals for X-ray diffraction study.

Electronic spectra. The colour of the trans- RuX_2L_2 solution is green while that of *cis*- RuX_2L_2 is bluish-green. The electronic spectra of the synthesized complexes were recorded in the range 800-250 nm. The complexes display multiple bands and shoulders (Table 2) in the aforesaid region. Representative spectra are displayed in Fig. 2. The transitions in the 700–550 nm region are assigned¹⁵ to metal-to-ligand charge-transfer $[t_2 \rightarrow \pi^*(L)]$ transitions. In our complexes multiple charge-transfer transitions may primarily originate²⁷⁻²⁹ from lower symmetry splitting of the metal level, the presence of different acceptor orbitals and from the mixing of singlet and triplet configurations in the excited state through spin-orbit coupling. In related complexes similar spectral patterns have also been reported.^{15,16,30} Here, we note some interesting trends in MLCT energies in the complexes. The higher energy band (ca 620 nm) together with the shoulder shift to higher energies on going from a trans to a cis configuration, but the energy of the lowest energy band (ca 675 nm) remains unaffected. On the other hand, on changing Cl to Br in a given pair of RuX_2L_2 (X = Cl, Br) the lowest energy band is blue shifted and the other band remains almost invariant. Transitions in the UV region are due to either intraligand $(n \rightarrow \pi^* \text{ and } \pi \rightarrow \pi^*)$ transitions or charge-transfer transitions involving energy



Fig. 2. Electronic spectra of trans-RuCl₂(L²)₂ (----), *cis*-RuCl₂(L²)₂, (----) and L² (-----) in CHCl₃.

levels which are higher in energies than the ligand LUMO.

Redox properties

The electron-transfer properties of the complexes have been studied voltammetrically in two solvents, viz. acetonitrile and chloroform, at a platinum electrode. Potential data are summarized in Table 4 and representative voltammograms are displayed in Fig. 3. All potentials are referenced to the saturated calomel electrode (S.C.E.).

In CH₃CN, the complexes display three one-elec-





Fig. 3. Segmented cyclic voltammograms of *trans*-RuCl₂(L^1)₂ (----) and *cis*-RuCl₂(L^1)₂ (----) in CH₃CN.

tron, nearly reversible to irreversible responses on the positive S.C.E. The first quasi-reversible oxidation occurs in the range 0.25-0.40 V, whereas the second and third irreversible electron transfers take place at very high positive potentials (>1.8 V). It may be noted here that the uncoordinated ligand, L^2 , also shows two irreversible oxidative responses at 1.54 and 1.93 V. It is, therefore, probable that the two successive oxidative responses occurring near 2.0 V are due to the ligand-based oxidation. The oxidation of coordinated imine linkages has been discussed³⁰ by others in a related ruthenium(II) system. We now consider the least positive oxidative quasi-reversible response which is assigned to the Ru^{III}/Ru^{II} couple in the complexes. At slow scan rates ($v < 100 \text{ mV s}^{-1}$) the peak-topeak separation of the cyclic voltammogram is 80-100 mV. On increasing the scan rate (v > 200 mV s^{-1}), and particularly on changing the solvent to CHCl₃, a significant deviation from reversibility is noticed. Exhaustive electrolyses have been performed for two representative cases at 0.5 V. These data confirm one-electron transfer of the couple.

The formal potentials collected in Table 4 show some interesting trends. The oxidation potential of the *cis* isomer is consistently slightly higher than that of the corresponding *trans* isomer. This has been generally observed^{20,31,32} in several other

Table 4. Cyclic voltammetric data" for RuX_2L_2 at a platinum electrode at the positive S.C.E.

	E	V)	
	CH ₃ CN		CHCl ₃
Compound	Ru ^{III} /Ru ^{II}	Ligand based oxidation	Ru ^{III} /Ru ^{II}
	,		
$2a^b$	0.31 (100)	1.88, 2.10	0.49 (400)
3a ^b	0.33 (90)	1.84, 2.10	0.51 (200)
4 a	0.40 (100)	1.86, 2.20	0.51 (390)
5a	0.40 (100)	1.84, 2.10	0.51 (170)
2b	0.29 (120)	с	0.47 (310)
3b	0.30 (100)	1.84, 2.20	0.47 (190)
4b	0.34 (120)	c	0.48 (360)
5b	0.36 (100)	1.81, 2.20	0.48 (170)
2c	0.36 (90)	c	0.55 (380)
3c	0.36 (90)	1.88, 2.30	0.55 (190)

^a Definitions of the symbols used are as in the text, all E values are quoted vs S.C.E., $v = 50 \text{ mV s}^{-1}$.

 ${}^{b}n = 0.98$ (for 2a) and 1.02 (for 3a), n = Q/Q'; where Q' is the calculated coulomb count for the transfer of one electron and Q is the observed coulomb count after exhaustive electrolysis; oxidation in each case was performed at 0.50 V vs S.C.E. in CH₃CN (0.10 M [NEt₄] [ClO₄]).

^c Solubility is very low, scanned up to +1.50 V.

cases. This effect is much more pronounced^{32a} in the complexes of strongly π -interacting ligands. It may thus be concluded that in the present complexes the π -interactions are of less importance. Moreover, the E_{298}° of the Ru^{III}/Ru^{II} couple in RuX_2L_2 is comparable to that in $RuX_2(bpy)_2$ (bpy = 2,2'-bipyridine). This similarity indicates that the ligand electrochemical parameter³³ of L is comparable to that of bpy. Interestingly, the formal potential data also reveal that the E_{298}° of the Ru^{III}/ Ru^{II} couple in $RuCl_2L_2$ depends on the nature of substitution (R) in the ligand L. The values decrease³⁴ with an increase in the electron-releasing power of the substituents. The plot of E_{298}° vs the Hammett substituent constant³⁵ (σ) is linear. Furthermore, the formal potentials of RuX_2L_2 show an increase on changing X from Cl to Br. Qualitatively this is attributed to a stabilization of ruthenium(II) by increased π -bonding in the dibromo complexes.

Finally, we note that the *cis* isomer of RuX_2L_2 is photoactive and undergoes light-induced reactions with several nucleophiles. Very recently it has been shown³⁶ that a mixed-ligand rhenium(I) (d^6) complex containing L¹ does show charge-transfer emission. This, in turn, appears to be a direct consequence of photo-induced reactions in our complexes. Studies to explore this area are continuing.

EXPERIMENTAL

Materials

The ligand (L) was generally obtained¹⁷ in situ by the condensation of pyridine-2-carboxaldehyde with an appropriate aromatic primary amine in C_2H_5OH . The ligand L^2 (1b) was prepared as before.^{15,17} Pyridine-2-carboxaldehyde was obtained from Merk, Schucdhardt. The salt $RuCl_3 \cdot nH_2O$ was obtained from Arora-Matthey, Calcutta, and it was digested thrice with concentrated HCl before use. The purification of dinitrogen gas and solvents and the preparation of the supporting electrolytes (TEAP, TBAP) for electrochemical work were performed as before.34 Ethanol was dried over fused CaO. Aromatic amines were either distilled over KOH or recrystallized before use. All other solvents and chemicals used for the preparative work were of reagent grade and were used as received.

Physical measurements

IR spectra were recorded (KBr discs, 4000–250 cm⁻¹) using a Perkin-Elmer IR-983 spectro-

photometer. Electronic spectra were recorded by the use of a Hitachi-330 spectrophotometer. ¹H NMR spectra (CDCl₃) were obtained with the use of a 500 MHz Bruker FT-NMR spectrometer, using TMS as an internal standard. The magnetic susceptibilities of the samples were measured on a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. Electrochemical measurements were carried out using a PAR model 370-4 electrochemistry system, which includes the 174A Polarographic Analyser, 175 Universal Programmer, RE0074 X-Y recorder, 173 Potentiostat, 170 Digital Cuolometer and 377A Cell system. The three electrode measurements were performed as before³⁴ using a planar Beckman model 39273, a platinum inlay working electrode for voltammetric experiments and a platinum wire gauge was used as a working electrode in coulometry.

The following σ -values for *para* substituents were used : Me, -0.17; H, 0.00; Cl +0.23.

Syntheses of complexes

The syntheses of complexes of the type RuX_2L_2 (X = Cl, Br) were achieved using general methods. Yields varied in the range 50–55%. Specific details are given for representative cases.

Dichlorobis(2-phenylpyridinecarboxaldimine) ruthenium(II) (2a and 3a). $RuCl_3 \cdot 3H_2O$ (0.520 g, 2 mmol) and excess LiCl (2 g) were dissolved in C_2H_5OH (20 cm³) and the mixture was refluxed for 15 min. To this red-brown solution a mixture of 2pyridinecarboxaldehyde (0.64 g, 6 mmol) and aniline (0.560 g, 6 mmol) in C_2H_5OH (25 cm³), which was refluxed separately for 30 min, was added. Immediately, a dark violet solution resulted, which was further refluxed for 2 h on a water bath. After cooling, dark crystals with a bronze-sheen were filtered off and washed with a little C_2H_5OH (5–10 cm³) and then ether. On TLC this compound showed two spots, indicating the presence of both trans (green, major fraction) and cis (bluish-green) isomers of $RuCl_2(L^1)_2$. The precipitate was then subjected to column chromatography on a silica gel column. First a green band was eluted with a 1:10 CH₃CN-CHCl₃ mixture. A second band, bluish green in colour, was eluted with a 2:10 CH₃CN-CHCl₃ mixture. These compounds were finally recrystallized from a 1:1 CHCl₃-C₆H₁₄ mixture.

Another fraction of isomeric $\text{RuCl}_2(L^1)_2$ was obtained from the violet filtrate. The filtrate was evaporated to dryness and washed thoroughly with water. The dried residue was then extracted with CHCl₃ (250 cm³). On addition of C₆H₁₄ to the concentrated CHCl₃ solution (25 cm³) a dark precipitate was obtained, which was subjected to column chromatography as described above to obtain pure green and bluish green isomers of $\text{RuCl}_2(L^1)_2$. Yields : **2a**, 35% ; **3a**, 19%. Found, **2a** : C, 53.9 ; H, 3.9 ; N, 10.4. **3a** : C, 54.0 ; H, 3.8 ; N, 10.5. Calc. for $C_{24}H_{20}N_4Cl_2Ru : C, 53.7$; H, 3.7 ; N, 10.4%.

Dibromobis(2-phenylpyridinecarboxaldimine) ruthenium(II) (**4a** and **5a**). These were prepared similarly with the exception that instead of LiCl, LiBr (2 g) was added to the solution of RuCl₃·3H₂O prior to the addition of an ethanolic solution of the ligand L¹. Isomeric purification was performed using the column chromatographic technique as described before RuCl₂(L¹)₂. Yields : **4a**, 32%; **5a**, 25%. Found, **4a** : C, 46.3; H, 3.2; N, 8.9. **5a** : C, 46.1; H, 3.2; N, 8.9. Calc. for C₂₄H₂₀N₄Br₂Ru : C, 46.1; H, 3.2; N, 9.0%.

Yields and analytical results for the other complexes are given below:

Yields: **2b**, 30%; **3b**, 21%. Found, **2b**: C, 55.1; H, 4.3; N, 9.7. **3b**: C, 55.4; H, 4.3; N, 9.8. Calc. for $C_{26}H_{24}N_4Cl_2Ru: C$, 55.3; H, 4.3; N, 9.9%.

Yields: **4b**, 24%; **5b**, 30%. Found, **4b**: C, 47.9; H, 3.8; N, 8.5. **5b**: C, 47.9; H, 3.8; N, 8.6. Calc. for $C_{26}H_{24}N_4Br_2Ru$: C, 47.8; H, 3.7; N, 8.6%.

Yields: **2c**, 35%; **3c**, 18%. Found, **2c**: C, 47.7; H, 3.1; N, 9.1. **3c**: C, 47.7; H, 3.1; N, 9.2. Calc. for $C_{24}H_{18}N_4Cl_4Ru: C$, 47.6; H, 3.0; N, 9.2%.

Preparation of **2b**, and **3b** from $\operatorname{RuCl}_3 \cdot \operatorname{3H}_2O$ and preformed L². A mixture of $\operatorname{RuCl}_3 \cdot \operatorname{3H}_2O$ (0.260 g, 1 mmol) and excess LiCl (2 g) in C₂H₅OH (20 cm³) was refluxed for 15 min. To this a solution of L² (0.590 g, 3 mmol) in C₂H₅OH was added and the mixture was further refluxed for 2 h. The rest of the procedure is similar to that described previously (**2a** and **3a**). Yields : **2b**, 32%; **3b**, 16%.

Acknowledgements—We are grateful to the Council of Scientific and Industrial Research, New Delhi, for financial support of this work. We acknowledge the technical assistance of the national NMR facilities, Tata Institute of Fundamental Research, Bombay, in running the 'H NMR spectra. We are also indebted to Professor S. N. Bhat for electronic spectral data.

REFERENCES

- (a) E. A. Seddon and K. R. Seddon, *The Chemistry* of Ruthenium. Elsevier, Amsterdam (1984); (b) K. R. Seddon, Coord. Chem. Rev. 1985, 67, 171 and refs therein.
- G. Wilkinson, Comprehensive Coordination Chemistry, Vol. 4, p. 277. Pergamon Press, Oxford (1987).
- 3. F. Calderazzo, C. Floriani, R. Henzi and F. L'Eplattenies, J. Chem. Soc. A 1969, 1378.

- 4. K. S. Finney and G. W. Evertt Jr, *Inorg. Chim. Acta* 1974, 11, 185.
- 5. J. R. Thornback and G. Wilkinson, J. Chem. Soc., Dalton Trans. 1978, 110.
- K. S. Murray, A. M. Vander Bergen and B. O. West, Aust. J. Chem. 1978, 31, 203.
- 7. S. Gopinathan, S. S. Despande and C. Gopinathan, Synth. React. Inorg. Met. Org. Chem. 1989, 19, 321.
- 8. G. K. Lahiri, S. Bhattacharya, B. K. Ghosh and A. Chakravorty, *Inorg. Chem.* 1987, 26, 4324.
- (a) M. M. Taqui Khan and S. Srivastava, *Polyhedron* 1988, 7, 1063; (b) M. M. Taqui Khan, D. Srinivas, R. I. Kureshy and N. H. Khan, *Inorg. Chem.* 1990, 29, 2320; (c) M. M. Taqui Khan, N. H. Khan, R. I. Kureshy, A. B. Boricha and Z. A. Shaikh, *Inorg. Chim. Acta* 1990, 170, 21; (d) M. M. Taqui Khan, D. Srinivas, R. I. Kureshy and N. H. Khan, *Polyhedron* 1991, 10, 2559.
- (a) A. K. Deb, P. C. Paul and S. Goswami, J. Chem. Soc., Dalton Trans. 1988, 2051; (b) A. K. Deb and S. Goswami, Polyhedron 1991, 10, 1799; (c) A. K. Deb, M. Kakoti and S. Goswami, J. Chem. Soc., Dalton Trans. 1991, 3249; (d) M. Kakoti, A. K. Deb and S. Goswami, Inorg. Chem. 1992, 31, 1302.
- A. K. Deb and S. Goswami, J. Chem. Soc., Dalton Trans. 1989, 1635.
- A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. Von Zelewsky, *Coord. Chem. Rev.* 1988, 84, 85.
- 13. T. J. Meyer, Pure Appl. Chem. 1986, 58, 1193.
- 14. J. V. Casper and T. J. Meyer, J. Am. Chem. Soc. 1983, 105, 5583.
- E. V. Dose and L. J. Wilson, *Inorg. Chem.* 1978, 17, 2600.
- P. Belser and A Von Zelewsky, *Helv. Chim. Acta* 1980, 63, 1675.
- S. K. Mandal and A. R. Chakravarty, *Polyhedron* 1992, 11, 823.
- 18. In the above reaction the stage at which the reduction of ruthenium(III) occurs is not clear to us but it is most likely that the addition of the ligands follows the reduction of the metal centre.
- H. Brunner and W. A. Herrmann, *Chem. Ber.* 1972, 105, 770.
- S. Goswami, A. R. Chakravarty and A. Chakravorty, Inorg. Chem. 1981, 20, 2246.
- 21. R. A. Krause and K. Krause, *Inorg. Chem.* 1980, 19, 2600.
- B. K. Ghosh, S. Goswami and A. Chakravorty, *Inorg. Chem.* 1983, 22, 3358.
- M. N. Ackermann, C. R. Barton, C. J. Deodene, E. M. Specht, S. C. Keill, W. E. Schreiber and H. Kim, *Inorg. Chem.* 1989, 28, 397.
- W. Kaein and S. Kohlmann, *Inorg. Chem.* 1987, 26, 68.
- E. V. Brown and G. R. Granneman, J. Am. Chem. Soc. 1975, 97, 621.
- A. K. Mahapatra, B. K. Ghosh, S. Goswami and A. Chakravorty, J. Ind. Chem. Soc. 1986, 53, 101.
- (a) B. J. Pankuch, D. E. Lacky and G. A. Crosby, J. Phys. Chem. 1980, 84, 2061; (b) A. Ceulemans

and L. G. Vanquickenborne, J. Am. Chem. Soc. 1981, 103, 2238.

- S. Decurtins, F. Felix, J. Ferguson, H. U. Gudel and A. Ludi, J. Am. Chem. Soc. 1980, 102, 4102.
- 29. E. M. Kober and T. J. Meyer, *Inorg. Chem.* 1982, 21, 3967.
- G. M. Brown, T. R. Weaver, F. R. Keene and T. J. Meyer, *Inorg. Chem.* 1976, 15, 190.
- N. Bag, G. K. Lahiri and A. Chakravorty, J. Chem. Soc., Dalton Trans. 1990, 1557; (b) A. Pramanik, N. Bag, G. K. Lahiri and A. Chakravorty, J. Chem. Soc., Dalton Trans. 1990, 3823; (c) A. Pramanik, N.

Bag, D. Ray, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.* 1991, **30**, 410.

- 32. (a) B. E. Bursten, J. Am. Chem. Soc. 1982, 104, 1299;
 (b) J. L. Walsh and B. Durham, Inorg. Chem. 1982, 21, 329.
- 33. A. B. P. Lever, Inorg. Chem. 1990, 29, 1271.
- 34. S. Goswami, R. N. Mukherjee and A. Chakravorty, Inorg. Chem. 1983, 22, 2825.
- 35. L. P. Hammett. *Physical Organic Chemistry*, 2nd edn. McGraw-Hill, New York (1970).
- 36. R. N. Dominey, B. Hauser, J. Hubbard and J. Dunham, *Inorg. Chem.* 1991, **30**, 4754.