

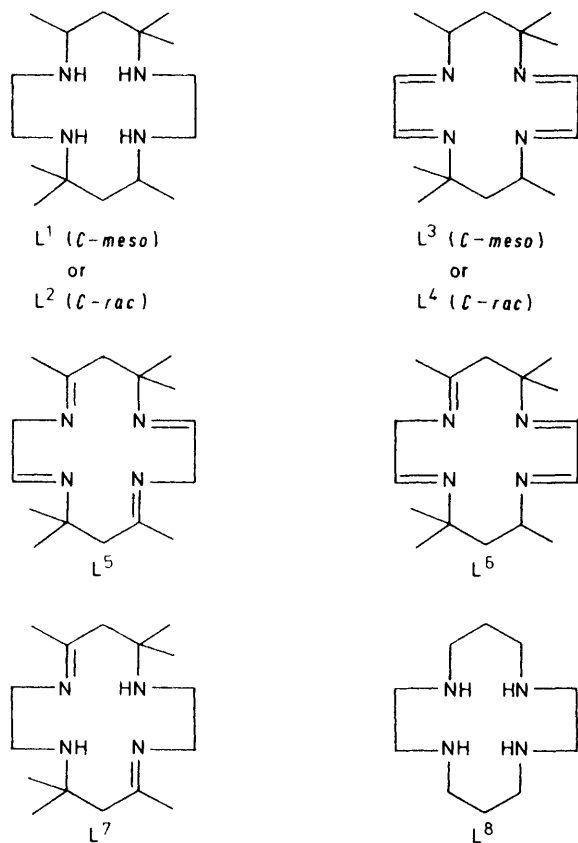
## Structural and Mechanistic Studies of Co-ordination Compounds. Part 28.<sup>1</sup> Some Octahedral Ruthenium Complexes of 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene produced by Oxidative Dehydrogenation Reactions

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Low-spin ruthenium(III) complexes,  $trans-[RuLCl_2]^+$ , where L represents *C-meso*- and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecaene ( $L^1$  and  $L^2$  respectively) have been found to undergo an eight-electron aerial oxidative dehydrogenation in ethanolic solution to the corresponding dichloro-complexes with unsaturated macrocycles  $L^3$  and  $L^4$ , where  $L^3$  and  $L^4$  represent *C-meso*- and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene respectively. A series of dianion-substituted complexes of the type  $trans-[RuL^3X_2]^{n+}$  ( $X = Br, n = 1$ ; and  $X = I, NCS, \text{ or } NO_2, n = 0$ ) have also been prepared. All these complexes have been characterized by i.r. and n.m.r. spectroscopy to contain two pairs of  $\alpha$ -di-imine units in the two five-membered chelate rings of the macrocyclic amine ligands. A mechanism for the oxidative dehydrogenation reaction is suggested. The electronic absorption spectra of these complexes are discussed.

THE activation of co-ordinated amine ligands towards oxidative dehydrogenation has been observed for some first- and second-row transition-metal amine complexes, such as those of iron(II),<sup>2-4</sup> nickel(II),<sup>5-6</sup> copper(II),<sup>7</sup> and ruthenium(II).<sup>8-12</sup> With the exception of Group 8

the amine macrocycle was effected by molecular oxygen under normal conditions of temperature and pressure.<sup>2</sup> Oxidative dehydrogenation of ruthenium amine complexes has been reported on several occasions, but the reactions have been observed for non-cyclic primary amines bound to ruthenium(II).<sup>8-12</sup> It has been suggested<sup>11,12</sup> that the reactions would probably begin with the oxidation of ruthenium(II) to ruthenium(III) which then rapidly oxidized the amine ligands by a combined intramolecular electron transfer and disproportionation reaction. However, no convincing evidence has ever been found to support the above mechanism. Whether the reactions took place directly on the amine ligands bound to a ruthenium(II) ion or through a reactive ruthenium(III) intermediate still remains uncertain. In any case, all the imine complexes prepared are in the ruthenium(II) state. We report here the first example in which such an oxidative dehydrogenation reaction is also possible for some saturated macrocyclic secondary amine complexes of ruthenium with the central metal ion clearly in the +3 state. The ease of aerial dehydrogenation of these complexes coupled with ready ligand substitution reactions of the dehydrogenated products provide a convenient route for the synthesis of a series of unsaturated macrocyclic amine complexes of ruthenium. This paper describes the preparation and characterization of  $trans-[RuL^3X_2]^{n+}$  ( $X = Cl \text{ or } Br, n = 1$ ; and  $X = I, NCS, \text{ or } NO_2, n = 0$ ) and  $trans-[RuL^4Cl_2]^+$  where  $L^3$  and  $L^4$  represent *C-meso*- and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene respectively.



metal complexes, drastic conditions are usually employed in the metal-promoted conversion of an amine to an imine. However, for  $trans-[FeL^1(NCCH_3)_2]^{2+}$ , where  $L^1$  represents *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, oxidative dehydrogenation of

### EXPERIMENTAL

$trans$ -Dichloro(*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene)ruthenium(III) perchlorate,  $trans-[RuL^3Cl_2][ClO_4]$ , was prepared by stirring an ethanolic solution of  $trans-[RuL^1Cl_2]^+$  in air for ca. 4 h during which the colour of the solution changed from light brown, through reddish brown, violet-red, to deep blue. It was preferable to have the starting  $trans-[RuL^1Cl_2]^+$  freshly prepared<sup>1</sup> by treating an ethanolic solution of  $L^1$  (ref. 13)

with a refluxing ethanolic suspension of  $K_2[RuCl_5(OH_2)]$  and filtering off the unreacted  $K_2[RuCl_5(OH_2)]$ . The hot *trans*- $[RuL^1Cl_2]^+$  solution was then cooled and used. The resulting blue solution was filtered (if necessary) and the filtrate was evaporated to dryness. The blue residue was dissolved in HCl (4 mol dm<sup>-3</sup>, 150 cm<sup>3</sup>) and the solution was refluxed for *ca.* 1 h during which the colour changed to reddish brown. The resulting solution was filtered while hot and the filtrate was concentrated to *ca.* 30 cm<sup>3</sup> using a rotary evaporator. Addition of an excess of Na[ClO<sub>4</sub>] crystallized out a reddish brown solid which was filtered off. The solid was recrystallized by adding Na[ClO<sub>4</sub>] to a hot concentrated HCl solution (*ca.* 4 mol dm<sup>-3</sup>, 80 °C) of the complex. The final product was filtered off, washed with a little ice-cold water and an ethanol–diethyl ether mixture, and dried *in vacuo* at 78 °C (yield 60%) (Found: C, 35.0; H, 5.3; Cl, 19.4; N, 10.3. Calc. for C<sub>16</sub>H<sub>28</sub>Cl<sub>3</sub>N<sub>4</sub>O<sub>4</sub>Ru: C, 35.1; H, 5.1; Cl, 19.5; N, 10.2%).

*trans*-Dichloro(*C*-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene)ruthenium(III) perchlorate, *trans*- $[RuL^4Cl_2][ClO_4]$ , was prepared in the same way, with a similar yield, as the *meso*-isomer starting with a freshly prepared ethanolic solution of *trans*- $[RuL^2Cl_2]^+$  (Found: C, 35.1; H, 5.4; Cl, 19.3; N, 10.0. Calc. for C<sub>16</sub>H<sub>28</sub>Cl<sub>3</sub>N<sub>4</sub>O<sub>4</sub>Ru: C, 35.1; H, 5.1; Cl, 19.5; N, 10.2%).

*trans*-Dibromo(*C*-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene)ruthenium(III) perchlorate, *trans*- $[RuL^3Br_2][ClO_4]$ , was prepared by heating a concentrated HBr solution (*ca.* 4 mol dm<sup>-3</sup>) of *trans*- $[RuL^3Cl_2][ClO_4]$  (0.5 g) on a steam bath for *ca.* 1.5 h. The solution was filtered while hot and excess of Na[ClO<sub>4</sub>] was added. On cooling, deep violet-red crystals appeared which could be recrystallized by adding Na[ClO<sub>4</sub>] to a hot concentrated HBr solution (*ca.* 4 mol dm<sup>-3</sup>, 80 °C) of the complex (yield 50%) (Found: C, 30.4; H, 4.7; Br, 24.8; N, 8.9. Calc. for C<sub>16</sub>H<sub>28</sub>Br<sub>2</sub>ClN<sub>4</sub>O<sub>4</sub>Re: C, 30.2; H, 4.4; Br, 25.1; N, 8.8%).

*trans*-(*C*-*meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene)di-isothiocyanatoruthenium(II)-water (1/1), *trans*- $[RuL^3(NCS)_2] \cdot H_2O$ , was prepared by refluxing an ethanolic solution (150 cm<sup>3</sup>) of *trans*- $[RuL^3Cl_2][ClO_4]$  (0.5 g) and excess of Na[NCS] (5 g) for *ca.* 3 h. The resulting blue solution was filtered while hot and the filtrate was evaporated slowly to dryness during which time a deep greenish blue microcrystalline solid gradually appeared. The solid was collected, washed with water (*ca.* 30 cm<sup>3</sup>) to remove the unreacted Na[NCS], then with a little ethanol–diethyl ether mixture, and was finally dried *in vacuo* at 78 °C. The complex so prepared was pure enough for most purposes but it could be recrystallized, if desired, by adding water to an ethanolic solution of the complex (yield 75%) (Found: C, 42.7; H, 6.2; N, 16.0; S, 12.6. Calc. for C<sub>18</sub>H<sub>30</sub>N<sub>6</sub>ORuS<sub>2</sub>: C, 42.3; H, 5.9; N, 16.4; S, 12.5%).

*trans*-(*C*-*meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene)di-iodoruthenium(II), *trans*- $[RuL^3I_2]$ , was prepared by essentially the same method as that for *trans*- $[RuL^3(NCS)_2] \cdot H_2O$  described above except that NaI was used. The complex was deep blue in colour (yield 70%) (Found: C, 30.0; H, 4.5; I, 40.3; N, 8.5. Calc. for C<sub>16</sub>H<sub>26</sub>I<sub>2</sub>N<sub>4</sub>Ru: C, 30.4; H, 4.4; I, 40.2; N, 8.9%).

*trans*-(*C*-*meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene)dinitroruthenium(II)-water (2/3), *trans*- $[RuL^3(NO_2)_2] \cdot 1.5H_2O$ , was prepared in the same way as the di-isothiocyanato-analogue by refluxing an ethanolic solution (150 cm<sup>3</sup>) of *trans*- $[RuL^3Cl_2][ClO_4]$  and an

excess of Na[NO<sub>2</sub>] (a saturated solution) for *ca.* 2 h during which time a deep violet-red solution was obtained. The solution was filtered while hot and the filtrate was quickly evaporated to dryness. The solid was stirred with an aqueous Na[NO<sub>2</sub>] solution (2 g in 15 cm<sup>3</sup>) and the insoluble violet-red product was collected, washed with water to remove the last trace of Na[NO<sub>2</sub>], and then with a little ethanol–diethyl ether mixture (yield 20%) (Found: C, 38.9; H, 5.9; N, 16.5. Calc. for C<sub>16</sub>H<sub>31</sub>N<sub>6</sub>O<sub>5.5</sub>Ru: C, 38.7; H, 6.2; N, 16.9%).

*Physical Measurements.*—Infrared spectra were recorded of Nujol mulls or KBr pellets on a Perkin-Elmer 577 spectrophotometer (200–4 000 cm<sup>-1</sup>). Electronic absorption spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer. Nuclear magnetic resonance spectra of freshly prepared CD<sub>3</sub>CN solutions were recorded with a JEOL FX90Q Fourier-transform n.m.r. spectrometer. Magnetic susceptibilities of solid samples were measured by the Gouy method using mercury tetra-(thiocyanato)cobaltate(II) as the calibrant.<sup>14</sup>

## RESULTS AND DISCUSSION

All the new complexes are highly coloured. The isomeric purity of each complex was confirmed by the observation that both the electronic absorption and i.r. spectra were unaffected by recrystallization and were unchanged on repeated preparation. All the ruthenium(III) complexes are low spin ( $\mu_{\text{eff}}$ <sup>298</sup> *ca.* 2.1 B.M.) \* and the ruthenium(II) complexes are diamagnetic. Conductivities in nitromethane confirmed that the ruthenium(II) species are non-electrolytes. Conductivities of the ruthenium(III) complexes could not be accurately determined because of their instability in solution.

The structure of the complexes was deduced from both i.r. and n.m.r. spectroscopy. For the new  $[RuL^3Cl_2][ClO_4]$  complex, the disappearance of the absorption at 3 190 cm<sup>-1</sup> for the  $\nu(N-H)$  stretch, present in the parent *trans*- $[RuL^1Cl_2][ClO_4]$ , confirms a complete conversion of the co-ordinated amine to an imine. With reference to the i.r. spectrum of *trans*- $[FeL^3(NCCH_3)_2]^{2+}$  (ref. 2), the presence of a band at 3 060 cm<sup>-1</sup> assignable to vinylic hydrogen and bands at 1 630 and 1 510 cm<sup>-1</sup> assignable to  $\nu(C=N)$  of  $\alpha$ -di-imines, absent in the starting *trans*- $[RuL^1Cl_2][ClO_4]$  complex, strongly suggests that the new dichloro-complex possesses an unsaturated macrocycle of structure L<sup>3</sup>. Although the technique of n.m.r. cannot easily be applied to this paramagnetic ruthenium(III) species, it may be used for its ruthenium(II) derivatives,  $[RuL^3X_2]$  (X = I, NCS, or NO<sub>2</sub>). As will be discussed later, such a n.m.r. study strongly supports the structure assigned to L<sup>3</sup>. A similar consideration of the i.r. spectrum of  $[RuL^4Cl_2][ClO_4]$ , which is nearly identical to that of  $[RuL^3Cl_2][ClO_4]$ , also confirmed the presence of two pairs of  $\alpha$ -di-imines in the two five-membered chelate rings of the L<sup>4</sup> macrocycle. However, the dichloro-complexes of L<sup>3</sup> and L<sup>4</sup> are clearly two distinctly different non-interconvertible isomers. Their electronic absorption spectra are slightly different, not in the number and positions of peaks but in their relative absorptivities. The pair of *trans*- $[RuL^iCl_2]^+$  (L = L<sup>1</sup> or

\* Throughout this paper: 1 B.M. =  $9.274 \times 10^{-24}$  A m<sup>2</sup>.

L<sup>2</sup>) complexes also differ slightly in their electronic absorption spectra.<sup>1</sup> Since oxidative dehydrogenation only occurs in the two five-membered chelate rings, it seems reasonable to assume that the stereochemistry at the two asymmetric carbon atoms of L<sup>1</sup> and L<sup>2</sup> is preserved in the dehydrogenated products. In other words, it would be expected that the L<sup>3</sup> complex would possess the *C-meso*-configuration while the L<sup>4</sup> complex would have the *C-rac* configuration.

As far as the geometrical configuration of these two dichloro-complexes is concerned, far-i.r. studies showed the presence of only one relatively intense  $\nu(\text{Ru}-\text{Cl})$  stretch at 350 cm<sup>-1</sup> for both complexes. The assignment of a *trans* configuration is, in fact, to be expected since these two complexes are derived from the corresponding *trans* L<sup>1</sup> and *trans* L<sup>2</sup> complexes respectively.

As for [RuL<sup>3</sup>Br<sub>2</sub>][ClO<sub>4</sub>], since this complex was prepared from *trans*-[RuL<sup>3</sup>Cl<sub>2</sub>]<sup>+</sup> by a simple ligand substitution reaction, it would most probably retain the same *trans* configuration with the same *C-meso*-unsaturated macrocycle L<sup>3</sup>. The i.r. spectrum with bands at 3 060, 1 600, and 1 500 cm<sup>-1</sup> supports this conclusion. The far-i.r. spectrum (200–400 cm<sup>-1</sup>) of this dibromo-complex is very weak and by comparing the spectrum with that of *trans*-[RuL<sup>3</sup>Cl<sub>2</sub>][ClO<sub>4</sub>], a weak band at 250 cm<sup>-1</sup> could be assigned to the  $\nu(\text{Ru}-\text{Br})$  stretch. Similarly, for the other three [RuL<sup>3</sup>X<sub>2</sub>] (X = I, NCS, or NO<sub>2</sub>) complexes, since they are all derived from *trans*-[RuL<sup>3</sup>Cl<sub>2</sub>]<sup>+</sup>, a *trans* configuration with the same unsaturated macrocycle L<sup>3</sup> is assumed for their structures. Again the i.r. spectra of these complexes invariably possess the vinylic hydrogen and  $\alpha$ -di-imine bands. Furthermore, the i.r. spectrum of *trans*-[RuL<sup>3</sup>(NO<sub>2</sub>)<sub>2</sub>].1.5-H<sub>2</sub>O has a strong band at 818 cm<sup>-1</sup> for a *N*-bonded  $\delta(\text{NO}_2)$  vibration. As for *trans*-[RuL<sup>3</sup>(NCS)<sub>2</sub>].H<sub>2</sub>O, a relatively intense band at 808 cm<sup>-1</sup> could be assigned to a *N*-bonded  $\nu(\text{C}-\text{S})$  vibration. There is no absorption in the region 690–720 cm<sup>-1</sup> where the *S*-bonded  $\nu(\text{C}-\text{S})$  vibration is expected.<sup>15</sup>

The n.m.r. spectra of the ruthenium(II) complexes are very similar to each other and to that of *trans*-[FeL<sup>3</sup>(NCCH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> (ref. 4). The spectrum of *trans*-[RuL<sup>3</sup>(NCS)<sub>2</sub>] in CD<sub>3</sub>CN is taken as representative for the following discussion. With reference to the spectrum of the iron(II) complex,<sup>4</sup> the n.m.r. spectrum of the ruthenium(II) complex can be conveniently divided into three regions of interest: 1–2, 2–8, and 8–9 p.p.m. In the 1–2 p.p.m. methyl region, three closely packed signals appeared at 1.54, 1.60, and 1.65 p.p.m. with relative intensities of 1:1:4. The first two signals were taken to represent the doublet of the two methyl groups attached to the asymmetric carbon atoms, while the more intense signal at 1.65 p.p.m. was assigned to the *gem*-dimethyl groups. In the 8–9 p.p.m. region, an absorption with splitting pattern centred at 8.70 p.p.m. was taken to represent the azomethine protons of the  $\alpha$ -di-imine functions. Finally in the 2–8 p.p.m. region, absorptions were observed for the two methine protons of the asymmetric carbons (broad signal at 4.50 p.p.m.)

and the four methylene protons at 2.14 p.p.m. The overall relative intensities of these signals are fully consistent with the number and types of protons expected for a macrocycle of structure L<sup>3</sup>: 1.54, 1.60 (six protons for the doublet); 1.65 (12); 2.14 (4); 4.50 (2); and 8.70 p.p.m. (4). The possibility of having the unsaturation at other positions is very unlikely. The absence of a  $\nu(\text{N}-\text{H})$  stretch at *ca.* 3 200 cm<sup>-1</sup> confirms that all four donating nitrogen atoms are involved in the unsaturation. If either of the two methyl groups originally attached to the asymmetric carbon atoms was involved in an imine linkage, such as that occurring in macrocycles of structures L<sup>5</sup> or L<sup>6</sup>, a methyl resonance at *ca.* 2.0–2.5 p.p.m. would have been observed by reference to the known n.m.r. spectra of cobalt(II),<sup>16</sup> nickel(II),<sup>17</sup> and iron(II)<sup>2,18</sup> complexes of macrocycle L<sup>7</sup>. Furthermore, these alternative structures would have given rise to a resonance at *ca.* 8.1 p.p.m. for azomethine protons of isolated imine functions<sup>4</sup> instead of the signal at 8.70 p.p.m. for the  $\alpha$ -di-imine functions for structure L<sup>5</sup> or in addition to such a  $\alpha$ -di-imine signal for structure L<sup>6</sup>.

All the macrocyclic tetraene complexes prepared appear to be indefinitely stable in the solid state. However, *trans*-[RuL<sup>3</sup>X<sub>2</sub>]<sup>+</sup> (X = Cl or Br) and *trans*-[RuL<sup>4</sup>Cl<sub>2</sub>]<sup>+</sup> are very unstable in solution except in the presence of the correspondingly strong acid HX (X = Cl or Br). A deep blue solution, characteristic of most ruthenium(II) L<sup>3</sup> complexes, would be formed when these ruthenium(III) complexes are dissolved in either basic or neutral aqueous solution, sometimes even in some organic solvents such as ethanol and dimethyl sulphoxide. The addition of concentrated HX restored the original colour of the ruthenium(III) complexes. The addition of concentrated HX to a blue solution originally derived from a L<sup>3</sup>-ruthenium(II) species would also generate the same dihalogeno-ruthenium(III) complexes. These observations seem to indicate that the dihalogeno-ruthenium(III) complexes can easily undergo reversible hydrolysis reactions. The hydrolysed product is easily reduced to the ruthenium(II) state. The addition of excess of HX would anate the hydrolysed product back to the dihalogeno-ruthenium(II) complex which is rapidly oxidized back to the ruthenium(III) state. Attempts have been made to identify the blue species obtained by dissolving either ruthenium(III) or ruthenium(II) L<sup>3</sup> complexes in water. When a saturated solution of Na[ClO<sub>4</sub>] was added to the blue solution, a blue perchlorate salt always resulted. Microanalysis of the blue solid fluctuated slightly, but in most cases the analytical results suggested the formula [RuL<sup>3</sup>(OH<sub>2</sub>)<sub>*m*</sub>][ClO<sub>4</sub>]<sub>2</sub> (*m* = 1 or 2). Unfortunately, attempts to purify this blue solid have been unsuccessful but its i.r. spectrum clearly showed the absence of a  $\nu(\text{N}-\text{H})$  stretch and it is diamagnetic. That the blue solution was a solution of a ruthenium(II) species was further supported by the following observation. When a piece of either nickel or zinc was immersed into a reddish brown acidified solution of ruthenium(III), such as *trans*-[RuL<sup>3</sup>Cl<sub>2</sub>]<sup>+</sup>, and was immediately withdrawn, the surface of the metal was

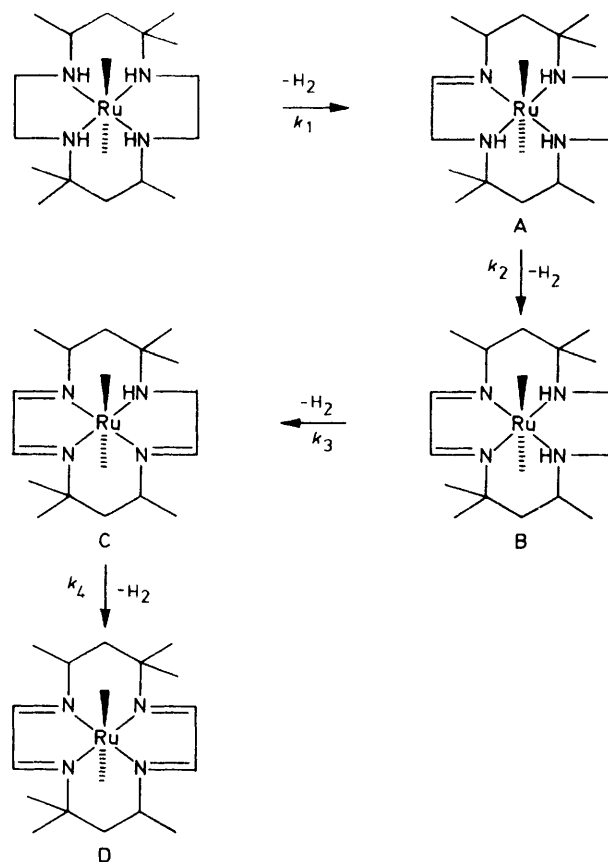
found to have been coated with a blue liquid film suggesting that a certain redox reaction had taken place converting the brown ruthenium(III) species into a blue compound.

For the synthesis of these tetraene complexes, various solvents have been tried but ethanol is found to be the best. The yields for the synthesis are usually rather good except for *trans*-[RuL<sup>3</sup>(NO<sub>2</sub>)<sub>2</sub>]. Molecular oxygen, derived from air, has been found to be most effective in bringing about the dehydrogenation reaction. Other oxidizing agents such as Br<sub>2</sub>, I<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> have been tried, but in each case only partial dehydrogenation was achieved. Reactions between *trans*-[RuL<sup>3</sup>Cl<sub>2</sub>]<sup>+</sup> and Na[N<sub>3</sub>] gave rise to a blue microcrystalline solid. An i.r. spectrum of this sample clearly indicated the presence of a co-ordinated azide as well as other features characteristic of the macrocycle L<sup>3</sup>. However, repeated elemental analysis on three independently prepared samples persistently gave a slightly lower nitrogen content than that required for the formula [RuL<sup>3</sup>(N<sub>3</sub>)<sub>2</sub>], although the percentages of carbon and hydrogen were acceptable (Found: C, 41.4; H, 6.1; N, 26.0. Calc. for C<sub>16</sub>H<sub>28</sub>N<sub>10</sub>Ru: C, 41.6; H, 6.1; N, 30.4%). Infrared spectra, however, did not show the presence of a co-ordinated dinitrogen or nitride ligand which might account for the lower percentage of nitrogen.

The ease of aerial dehydrogenation of the L<sup>1</sup> and L<sup>2</sup> ruthenium complexes is an outstanding feature. However, the corresponding *trans*-[RuL<sup>8</sup>Cl<sub>2</sub>]<sup>+</sup> complex is very stable towards aerial oxidation. Indeed, the L<sup>8</sup> complex can be kept in water and ethanol for several hours without any observable changes. For both the L<sup>1</sup> and the L<sup>2</sup> complexes the colour of the solution rapidly turned reddish brown and violet-blue on exposure to air. The reaction was found to be retarded by most acids, such as trichloroacetic, toluene-*p*-sulphonic, hydrochloric, and sulphuric acid. No aerial dehydrogenation was found over a period of 2 days when the complex solution was treated with one of the above acids. Oxalic and fumaric acids were found to be less effective, while acetic acid could not stop the aerial dehydrogenation. Therefore, the dehydrogenation reaction probably goes through an amido-intermediate since these reactions are also facilitated by additional bases. Although Taube and his co-workers<sup>11</sup> suggested that oxidative dehydrogenation of ruthenium(II) amine complexes would probably begin with the oxidation of ruthenium(II) to ruthenium(III) which then, by intramolecular electron transfer, oxidized the amine ligand to an imine, no conclusive evidence has been found to support their mechanism. Indeed, all reports on metal-promoted oxidation of amine ligands were limited to divalent metal complexes. The present report is the first example to demonstrate that aerial dehydrogenation also occurs very readily for trivalent metal complexes.

Although the end product of the oxidative dehydrogenation reaction of *trans*-[RuL<sup>1</sup>X<sub>2</sub>]<sup>+</sup> (X = Cl or Br) has been shown to be *trans*-[RuL<sup>3</sup>X<sub>2</sub>]<sup>+</sup>, it is possible that the oxidation may involve the intermediate formation of

complexes with macrocycles L<sup>5</sup> or L<sup>6</sup>. It has been reported<sup>2</sup> that iron(II) complexes of L<sup>5</sup> underwent tautomerization to produce the corresponding iron(II) complexes of L<sup>3</sup>. To eliminate this possibility, an n.m.r. study of the oxidative dehydrogenation of *trans*-[RuL<sup>1</sup>I<sub>2</sub>] has been carried out. The complex *trans*-[RuL<sup>1</sup>I<sub>2</sub>] was dissolved in CDCl<sub>3</sub> and air was admitted. The solution, originally yellowish brown in colour, gradually turned reddish brown and finally deep blue. The course of the reaction was followed by n.m.r. Initially, the spectrum of *trans*-[RuL<sup>1</sup>I<sub>2</sub>] exhibited a broad peak at 1.20 p.p.m. corresponding to the six methyl groups of macrocycle L<sup>1</sup>. There was no absorption in the 8–9 p.p.m. region. As the reaction proceeded, the intensity of the peak at 1.20 p.p.m. decreased and several new signals appeared. Perhaps the most significant feature of the n.m.r. spectrum of the partially oxidized species is that a doublet at 8.64 and 8.75 p.p.m. corresponding to the  $\alpha$ -di-imine function gradually developed and new methyl signals appeared in the 1.50–1.70 p.p.m. region. Absorptions corresponding to both an isolated imine proton, HC=N, at *ca.* 8.1 p.p.m.



and a CH<sub>3</sub>C=N methyl in the region 2.0–2.5 p.p.m. never appeared during the entire course of the reaction. The position of the  $\alpha$ -di-imine doublet remained essentially unchanged while the methyl signals finally developed into a doublet at 1.50 and 1.60 p.p.m. and a singlet at 1.72 p.p.m. with relative intensities of 1 : 2. Obviously,

Visible and u.v. absorption spectra of some *trans*-ruthenium macrocyclic tetraene complexes

Complex	Solvent	$\lambda_{\max.}/\text{nm}^a$
[RuL <sup>3</sup> Cl <sub>2</sub> ][ClO <sub>4</sub> ]	HCl <sup>b</sup>	525br (2 150), 496br (2 450), 472br (sh) (2 090), 414 (3 180), 355 (2 610), 339br (2 260), ca. 297br (sh) (2 800)
[RuL <sup>4</sup> Cl <sub>2</sub> ][ClO <sub>4</sub> ]	HCl <sup>b</sup>	525br (sh) (1 640), 494br (2 060), 472br (sh) (1 940), 413 (3 050), 355 (2 160), 336br (2 080), ca. 300br (sh) (2 610)
[RuL <sup>3</sup> Br <sub>2</sub> ][ClO <sub>4</sub> ]	HBr <sup>b</sup>	505 (4 830), 355br (2 540)
[RuL <sup>3</sup> I <sub>2</sub> ]	CHCl <sub>3</sub>	635 (6 260), ca. 590br (sh) (3 390), ca. 545br (sh) (2 300), 355 (3 450)
	CH <sub>3</sub> NO <sub>2</sub> <sup>c</sup>	629 (5 960), ca. 590br (sh) (3 420), ca. 545br (sh) (2 220)
[RuL <sup>3</sup> (NCS) <sub>2</sub> ·H <sub>2</sub> O]	CHCl <sub>3</sub>	631br (5 930), 588br (5 590), ca. 527br (sh) (3 070), ca. 485br (sh) (1 500), ca. 338br (sh) (2 280)
	CH <sub>3</sub> NO <sub>2</sub> <sup>c</sup>	620br (5 570), ca. 584br (sh) (5 300), ca. 520br (sh) (2 920), ca. 487br (sh) (1 580)
[RuL <sup>3</sup> (NO <sub>2</sub> ) <sub>2</sub> ·1.5H <sub>2</sub> O]	CHCl <sub>3</sub>	541 (7 560), ca. 506br (sh) (4 960), ca. 475br (sh) (3 070), 350br (4 130), ca. 312br (3 660)
	CH <sub>3</sub> NO <sub>2</sub> <sup>c</sup>	541 (7 200), ca. 509 (sh) (4 740), ca. 474 (2 910)

<sup>a</sup> Molar absorption coefficients ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) are given in parentheses; abbreviations: br, broad; sh, shoulder. <sup>b</sup> In 6 mol dm<sup>-3</sup> HCl (or HBr). <sup>c</sup> Solvent CH<sub>3</sub>NO<sub>2</sub> starts absorbing after 370 nm and, therefore,  $\lambda_{\max.}$  values below 380 nm were not recorded in this solvent system.

the doublet could be assigned to the methyl groups attached to the two asymmetric carbon atoms while the singlet is assigned to the two pairs of *gem*-dimethyl groups of the oxidized macrocycle L<sup>3</sup>. This observation was consistent with the reaction scheme (shown above) with  $k_2$  and  $k_4$  much greater than  $k_1$  and  $k_3$  respectively. There was no obvious accumulation of species A and C otherwise a triplet corresponding to the isolated HC=N function would have been observed near 8.1 p.p.m. According to such a mechanism, it would be expected that the corresponding *trans*-[RuL<sup>3</sup>Cl<sub>2</sub>]<sup>+</sup> complex would have been sensitive to aerial dehydrogenation. The fact that it is stable towards aerial dehydrogenation seems to indicate that the methyl groups on L<sup>1</sup> and L<sup>2</sup> may have some accelerating effects on the reactivity but the reason behind this is unknown.

The electronic absorption spectra of the ruthenium(II) tetraene complexes (Table) are dominated by the intense metal-to-ligand charge-transfer transitions. The lowest-energy  $\lambda_{\max.}$  values of *trans*-[RuL<sup>3</sup>(NCS)<sub>2</sub>] and *trans*-[RuL<sup>3</sup>I<sub>2</sub>] are nearly the same but they are quite different from that of *trans*-[RuL<sup>3</sup>(NO<sub>2</sub>)<sub>2</sub>]. These transitions, which are slightly solvent dependent, are almost certainly associated with charge transfer from the metal  $t_{2g}$  type orbitals to the  $\pi^*$  level of the  $\alpha$ -di-imine units of L<sup>3</sup>. These transitions, therefore, would be quite independent of the nature of non- $\pi$ -accepting or very weakly  $\pi$ -accepting axial ligands. Since NO<sub>2</sub><sup>-</sup> is an extremely good Lewis acid and a good  $\pi$  acceptor, it would further stabilize the metal  $t_{2g}$  level by the partial removal of the  $t_{2g}$ <sup>6</sup> electrons from the ruthenium(II) centre in the ground state. Consequently, the  $t_{2g} \rightarrow \pi^*_{\alpha\text{-di-imine}}$  transition would probably take place at a higher frequency. This might explain the observation that the  $\lambda_{\max.}$  value of *trans*-[RuL<sup>3</sup>(NO<sub>2</sub>)<sub>2</sub>] is much smaller than that of *trans*-[RuL<sup>3</sup>X<sub>2</sub>] (X = NCS or I).

The electronic spectra of *trans*-[RuL<sup>3</sup>X<sub>2</sub>]<sup>+</sup> (X = Cl or Br) (Table) are more complicated than those of their ruthenium(II) derivatives. Here, two different kinds of ligand-to-metal ( $\pi_x \rightarrow t_{2g}$  and  $\pi_{\alpha\text{-di-imine}} \rightarrow t_{2g}$ ) transitions are expected. A direct comparison between their spectra indicated that the most intense peak for *trans*-[RuL<sup>3</sup>Cl<sub>2</sub>]<sup>+</sup> at 413 nm and for *trans*-[RuL<sup>3</sup>Br<sub>2</sub>]<sup>+</sup> at 505 nm might be assigned to  $\pi_x \rightarrow t_{2g}$  transitions. The assignment is

supported by the red shift of the transitions from the chloro- to the bromo-complexes and by the observation that most *trans*-dichloro-saturated tetramine ruthenium(III) complexes exhibit a  $\pi_{\text{Cl}} \rightarrow t_{2g}$  band in the region 350–420 nm and their corresponding dibromo-complexes in the region 410–500 nm.<sup>1,19</sup> For *trans*-[RuL<sup>3</sup>-Cl<sub>2</sub>]<sup>+</sup>, a broad transition comprising three shoulders is observed at ca. 500 nm. This is probably due to a  $\pi_{\alpha\text{-di-imine}} \rightarrow t_{2g}$  transition. Such a transition would be expected to be independent of the nature of the halogeno-ligands. Therefore, both  $\pi_{\text{Br}} \rightarrow t_{2g}$  and  $\pi_{\alpha\text{-di-imine}} \rightarrow t_{2g}$  transitions in *trans*-[RuL<sup>3</sup>Br<sub>2</sub>]<sup>+</sup> might overlap extensively near 500 nm. The much greater intensity of this dibromo-peak and the relatively wide half-band width support this assignment.

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