Synthesis, Characterisation, and Reactivity of New Mononitrosyl Complexes of Ruthenium containing 2-(Arylazo)pyridines: Examples of Strongly Electrophilic Nitrosyls

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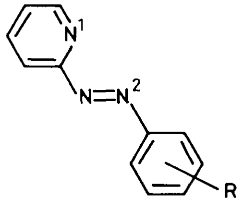
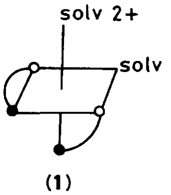
A high-yield synthetic route to ruthenium mononitrosyls of type $[Ru(NO)(NO_2)L_2]^{2+}$ (**3**) [L = 2-(arylazo)pyridine] from the dinitro precursor, $[Ru(NO_2)_2L_2]$ (**2**) is described. Complexes (**3**) were isolated as crystalline perchlorate salts. In an alkaline medium, (**3**) regenerates (**2**). The electronic spectra of complexes (**2**) and (**3**) exhibit allowed metal-to-ligand charge-transfer transitions in the visible region, 400—550 nm. The nitrosyls absorb at high wavenumbers[ν(NO) *ca.* 1 950 cm^{-1}] in the i.r. spectra. All the complexes are electroactive. Secondary oxidation of co-ordinated nitrite in (**2**) occurs after electrochemical metal oxidation. In the case of complexes (**3**), two successive one-electron reductions have been observed at relatively high positive potentials.

The electrophilic behaviour of co-ordinated nitric oxide (NO) has been of recent interest [1–14] in ruthenium nitrosyl chemistry. It has been shown that those nitrosyls having a sufficiently high degree of nitrosonium ion (NO^+) character and generally showing relatively high ν(NO) (*e.g.* > 1 850 cm^{-1}) are susceptible to nucleophilic attack. Synthesis of nitrosyls containing electrophilic NO is, however, an important pre-requisite for studying the above reactions. The goal of the present work was to study the nitrosyl chemistry of ruthenium complexes containing the ligand 2-(arylazo)pyridine, L. Although it was recently remarked in passing [15] that it might not be possible to achieve the synthesis of such nitrosyls, because of the very high π acidity [15–17] of L, we thought the synthesis could be achieved under appropriate conditions. The present report describes the successful synthesis, characterisation, and electron-transfer behaviour of mononitrosyl complexes of type $[Ru(NO)(NO_2)L_2][ClO_4]_2$ as well as their precursor dinitro species, $[Ru(NO_2)_2L_2]$. The three ligands used are abbreviated as L^1—L^3.

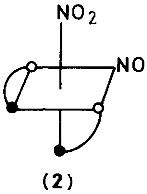


	R
L^1	H
L^2	*m*-Me
L^3	*p*-Me

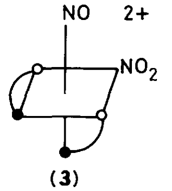


(1)

● : N^2



(2)



(3)

Results and Discussion

Stereochemistry of Starting Material and Synthesis.—The cationic disolvento complex, $[Ru(solv)_2L_2]^{2+}$ exists [16b] in two isomeric forms. Both have the *cis*-$Ru(solv)_2$ moiety. Stereochemistries of isomers having a RuL_2 moiety have been defined.[16] Thus, isomer (**1**) of $[Ru(solv)_2L_2]^{2+}$ is *trans*, *cis*, or simply *tc*. The *tc* isomer of $[Ru(solv)_2L_2]^{2+}$ undergoes stereoretentive † nucleophilic displacement in the presence of an excess of sodium nitrite [equation (1)] to produce *tc*-$[Ru(NO_2)_2L_2]$ (**2**) which was used as the starting material for the synthesis of the desired nitrosyl complex. Proton-assisted conversion of (**2**) into the cationic nitrosyl complex, $[Ru(NO)(NO_2)L_2]^{2+}$ (**3**), takes place in highly acidic media [equation (2)]. A 1 : 1 mixture of ice-cold concentrated HNO_3 (10 mol dm^{-3}) and concentrated $HClO_4$ (10 mol dm^{-3}) was found to be the most effective for isolation of (**3**) as its perchlorate salt. Since the reaction of H^+ with one of the peripheral NO_2 groups is the key step in reaction (2) it is logical to assume that the gross stereochemistry of the RuL_2 moiety in (**3**) is retained as it was in (**2**). It is relevant that reaction (2) does not take place in dilute aqueous acid. However, the reactions of both complexes (**2**) and (**3**) with boiling aqueous acid (*ca.* 1 mol dm^{-3}) proceed slowly but smoothly to yield (**1**; solv = H_2O).

$$tc\text{-}[Ru(solv)_2L_2]^{2+} + 2\,NO_2^- \longrightarrow tc\text{-}[Ru(NO_2)_2L_2] + 2\,solv \quad (1)$$

$$tc\text{-}[Ru(NO_2)_2L_2] + 2\,H^+ \longrightarrow tc\text{-}[Ru(NO)(NO_2)L_2]^{2+} + H_2O \quad (2)$$

The complexes are all diamagnetic as evidenced by the results of magnetic susceptibility measurements. While the perchlorate of (**3**) behaves as a 1 : 2 electrolyte,[18] the dinitro compound (**2**) is a non-electrolyte in acetonitrile.

Spectra.—Selected i.r. data together with electronic spectral data for the newly synthesised complexes are given in the

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† The complexes $[Ru(NO_2)_2(L^2)_2]$ and $[Ru(NO_2)_2(L^3)_2]$ show a sharp methyl n.m.r. signal at 2.13 and 2.07, respectively, in $CDCl_3$. The corresponding disolvento species show [16b] a single methyl signal at *ca.* 2.14 in $(CD_3)_2SO$. Thus, the RuL_2 fragment of (**2**) retains the symmetry of the disolvento precursor.

Table 1. Cyclic voltammetric data[a] for *tc*-$[Ru(NO_2)_2L_2]$ (**2**) and *tc*-$[Ru(NO)(NO_2)L_2][ClO_4]_2$ (**3**) at a platinum electrode

Compound	Responses to positive potential of the s.c.e.[b] E°_{298}/V(ΔE_p/mV)	Ligand reductions E°_{298}/V(ΔE_p/mV)
(**2a**) *tc*-$[Ru(NO_2)_2(L^1)_2]$	1.40,[c] 1.63(70)	0.50(100), 0.92(200)
(**2b**) *tc*-$[Ru(NO_2)_2(L^2)_2]$	1.38,[c] 1.60(80)	0.50(100), 0.92(220)
(**2c**) *tc*-$[Ru(NO_2)_2(L^3)_2]$	1.35,[c] 1.59(80)	0.53(80), 0.91(220)
(**3a**) *tc*-$[Ru(NO)(NO_2)(L^1)_2][ClO_4]_2$	0.72(60), 0.17[d]	*e*
(**3b**) *tc*-$[Ru(NO)(NO_2)(L^2)_2][ClO_4]_2$	0.76(60), 0.17[d]	0.38(80), 0.51(70)
(**3c**) *tc*-$[Ru(NO)(NO_2)(L^3)_2][ClO_4]_2$	0.71(70), 0.15[d]	*e*

[a] Cyclic voltammetry was carried out in MeCN at 298 K using 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ as a supporting electrolyte. The reported data correspond to scan rate v = 50 mV s^{-1}. [b] For complexes (**2a**)—(**2c**) the responses are metal centred, whereas for (**3a**)—(**3c**) they are mainly localised at the co-ordinated NO. [c] Anodic peak potential with no cathodic counterpart. [d] Cathodic peak potential with no anodic counterpart. [e] Not studied.

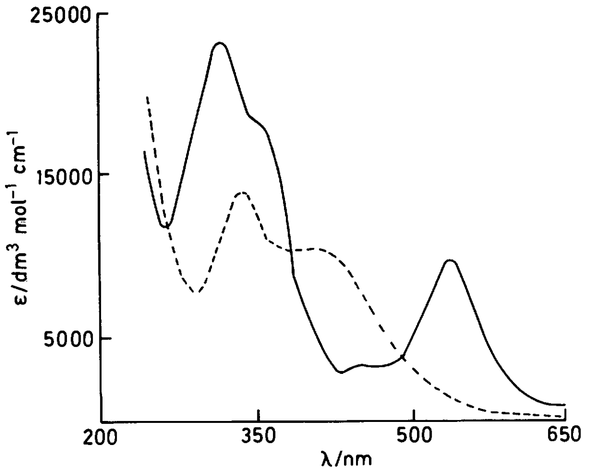

Figure 1. Electronic spectra of *tc*-$[Ru(NO_2)_2(L^1)_2]$ in dichloromethane (——) and of *tc*-$[Ru(NO)(NO_2)(L^3)_2][ClO_4]_2$ in acetonitrile (– – – –)

Experimental section. One of the most significant observations is the consistent appearance of a strong band at *ca.* 1 950 cm^{-1} in the i.r. spectra of complexes (**3**) which is conspicuously absent in (**2**). Evidently, this is due to the stretching mode[7,19–21] [v(NO)] of the co-ordinated NO. Such a high value of v(NO) indicates[20] that formally a linear NO^+ is co-ordinated to the ruthenium centre. Also it is noteworthy that the N=N stretching modes of both (**2**) and (**3**) appear at relatively higher frequencies compared to other ruthenium complexes,[15,16] having a RuL_2^{2+} moiety. While complexes (**2**) display a strong band at *ca.* 1 360 cm^{-1}, (**3**) show a strong band at *ca.* 1 840 cm^{-1}, both of which are assignable[20] to v(NO_2). The positions of these bands indicate that nitrite is co-ordinated through nitrogen, rather than through one of the oxygens.

Solution electronic spectra of *tc*-$[Ru(NO_2)_2(L^1)_2]$ and *tc*-$[Ru(NO)(NO_2)(L^3)_2][ClO_4]_2$ are displayed in Figure 1. We assign[15,16] the lowest-energy band in the visible region to a metal-to-ligand charge-transfer (m.l.c.t.) transition. This band is blue shifted from *ca.* 540 nm for (**2**) to *ca.* 410 nm for (**3**). Nitrosyl co-ordination stabilises the t_2 level of ruthenium better than does NO_2^- and in turn increases the m.l.c.t. energy. We note here that the m.l.c.t. band of (**2**) is associated with a shoulder at *ca.* 455 nm (Figure 1). Such a pattern confirms[16a] the *cis* geometry of complexes (**2**).

Redox Properties.—The electron-transfer behaviour of the complexes in acetonitrile solution was examined by cyclic voltammetry at a platinum electrode. Several one-electron quasi-reversible to irreversible responses were observed to negative potentials of the saturated calomel electrode (s.c.e.) (Table 1) due to ligand reductions localised[16] at the azo group. Our interest was the redox processes to positive potentials of the s.c.e.

Table 2. Comparison of $E°(1)$ (MeCN) and v(NO) (KBr)

Compound	v(NO)/cm^{-1}	$E°(1)$/V
NO^+	2 220[19]	0.74[26,*]
tc-$[Ru(NO)(NO_2)(L^1)_2]^{2+}$	1 950	0.72
$[Ru(NO)(NO_2)(bipy)_2]^{2+}$	1 935	0.33[23]
$[Ru(NO)Cl(py)_4]^{2+}$	1 910[9]	0.10[9]
$[Ru(NO)(NH_3)_5]^{3+}$	1 913[24]	−0.36[25]

* In an aqueous acidic medium, HNO_2 can be considered to be free NO^+ (T. A. Turney and G. A. Wright, *Chem. Rev.*, 1959, **59**, 497).

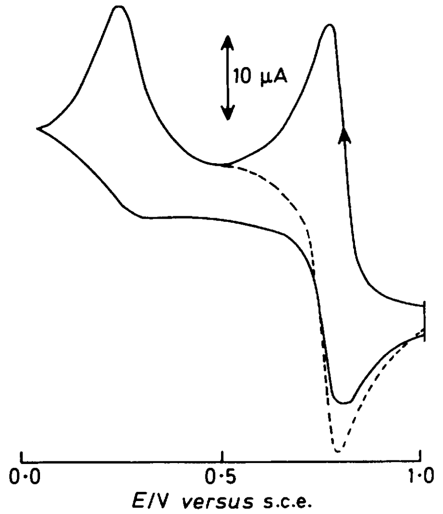

Figure 2. Cyclic voltammogram of *tc*-$[Ru(NO)(NO_2)(L^2)_2][ClO_4]_2$ (——) at a scan rate of 50 mV s^{-1} in acetonitrile. The broken line shows a voltammogram where the cathodic scan was reversed before reaching the second reduction wave

(*a*) *tc*-$[Ru(NO_2)_2L_2]$ (**2**). The dinitro complexes display one-electron irreversible oxidative responses at *ca.* 1.40 V followed by quasi-reversible responses at *ca.* 1.60 V (Table 1). These responses are closely spaced. The nature of the voltammogram indicates[22] that there is an initial oxidation of ruthenium(II) to ruthenium(III) [equation (3)], which then undergoes some other chemical transformations. The response at higher potential is most probably due to electron transfer of ruthenium(II) species, formed by secondary chemical transformation of the transient (**2′**). The initial oxidation of complexes (**2**) occurs at a very high positive potential and the chemical transformations also occur very rapidly.

$$\underset{(\mathbf{2})}{tc\text{-}[\mathrm{Ru(NO_2)_2L_2}]} \longrightarrow \underset{(\mathbf{2'})}{tc\text{-}[\mathrm{Ru(NO_2)_2L_2}]^+} + e^- \quad (3)$$

(*b*) *tc*-$[Ru(NO)(NO_2)L_2][ClO_4]_2$ (**3**). A typical cyclic voltammogram of *tc*-$[Ru(NO)(NO_2)(L^2)_2][ClO_4]_2$ is shown in Figure 2. All the nitrosyl complexes showed a one-electron reversible reduction with formal potential (E°_{298}) at *ca.* 0.70 V. The E°_{298} value for the reversible wave has been labelled as $E^\circ(1)$. A second one-electron irreversible cathodic response with cathodic peak potential ($E_{p,c}$) at *ca.* 0.17 V, labelled as $E_{p,c}(2)$, was also observable (Figure 2, Table 1). A comparison of our data with those for other analogous systems[9,23–25] leads us to suggest the occurrence of successive two-electron reductions at the {RuNO} moiety [equations (4) and (5)]. Irreversibility of the couple (5) indicates that the two-electron reduced product of (**3**) is not stable and undergoes some chemical transformations. No voltammetric response corresponding to the oxidation of (**3**) was observed up to 2.0 V.

$$tc\text{-}[\mathrm{Ru(NO)(NO_2)L_2}]^{2+} + e^- \rightleftharpoons tc\text{-}[\mathrm{Ru(NO)(NO_2)L_2}]^+ \quad (4)$$

$$tc\text{-}[\mathrm{Ru(NO)(NO_2)L_2}]^{+} + e^- \longrightarrow tc\text{-}[\mathrm{Ru(NO)(NO_2)L_2}] \quad (5)$$

In this context it is worthwhile to compare the $E^\circ(1)$ and $\nu(NO)$ of complexes (**3**) with those of some of the earlier reported systems (Table 2). Thus, in the series, *tc*-$[Ru(NO)(NO_2)L_2]^{2+}$ (**3**), $[Ru(NO)(NO_2)(bipy)_2]^{2+}$ (bipy = 2,2′-bipyridine), $[Ru(NO)Cl(py)_4]^{2+}$ (py = pyridine), and $[Ru(NO)(NH_3)_5]^{3+}$ (**3**) have the highest $\nu(NO)$ and are much better oxidants. It is also evident that the replacement of two bipy by two L leads to dramatic augmentation of reduction potentials of the co-ordinated NO. This is attributed to the much stronger π-acceptor character of L compared to that of bipy. Further, the value of $E^\circ(1)$ for (**3**) is very close to the reduction potential[26] of unco-ordinated NO^+. This implies that the electrophilicity of the co-ordinated NO in complexes (**3**) is comparable to that of free NO^+. The insignificant π interaction of NO in the present nitrosyls is surely responsible for such a high $E^\circ(1)$. To our knowledge, the observed reduction potentials are the highest ever reported in ruthenium mononitrosyl chemistry.

Chemical Reactivity.—The orange *tc*-$[Ru(NO)(NO_2)L_2]^{2+}$ ions are predominant in a very high acidic ($[H^+] > 1.0$ mol dm^{-3}) medium. In moist environments they revert to the corresponding dinitro complexes, *tc*-$[Ru(NO_2)_2L_2]$. Reaction (6) is reversible and each of the species is interconvertible by adjustment of the pH of the medium. Unfortunately, the equilibrium constant, *K*, of reaction (6) could not be measured because of the insolubility of (**2**) in water. However, instantaneous conversion of complexes (**3**) into (**2**) even in a neutral aqueous medium indicates that *K* must be very high. The net chemical conversion of (**3**) into (**2**) involves donation of an electron pair from O^{2-} to the co-ordinated nitrosyl group. Thus, the high positive reduction potentials of the present nitrosyls are believed to be one of the crucial factors for such facile conversion. It is to be noted that the preliminary results of reactions of (**3**) with alcohols, tertiary phosphines, and also with aromatic amines are encouraging and studies of these reactions are underway.

$$tc\text{-}[\mathrm{Ru(NO)(NO_2)L_2}]^{2+} + OH^- \rightleftharpoons tc\text{-}[\mathrm{Ru(NO_2)_2L_2}] + H^+ \quad (6)$$

Conclusions

The heretofore unsuccessful synthesis of *tc*-$[Ru(NO)(NO_2)L_2][ClO_4]_2$ (**3**) has now been achieved in good yield. A more pronounced nitrosonium ion character of the co-ordinated NO group in (**3**), as compared to that in any other ruthenium mononitrosyl complex reported, is in total agreement with its physico-chemical data and reactivity.

Experimental

Materials.—The ligand was synthesised as before.[27] Dinitrogen was purified by bubbling it through an alkaline dithionite reducing solution. The purification and preparation of solvents and the supporting electrolyte for electrochemical work was as before.[16] All other chemicals and solvents for preparative work were of reagent grade and were used without further purification.

Physical Measurements.—Spectroscopic data were obtained with the following instruments: electronic, Hitachi 330 spectrophotometer; i.r. (KBr disc, 4000—600 cm^{-1}), Perkin-Elmer IR-297 spectrophotometer; ^{1}H n.m.r. ($CDCl_3$), Varian EM 390. Solution electrical conductivity was measured using a Elico CM82T conductivity bridge with a solute concentration of *ca.* 10^{-3} mol dm^{-3}. Magnetic susceptibilities were measured with a PAR vibrating-sample magnetometer (model 155) fitted with a Walker Scientific Magnet (model L75 FBAL). Cyclic voltammetric measurements were carried out with the help of a PAR model 370-4 electrochemistry system: 174A, polarographic analyser 175, universal programmer, RE0074, and XY recorder. All experiments were done under a dinitrogen atmosphere in a three-electrode configuration by using a planar Beckman model 39273 platinum electrode as the working electrode. All results were collected at 298 ± 1 K and are referenced to a saturated calomel electrode (s.c.e.). The reported potentials are uncorrected for the junction contribution.

Syntheses.—The salt *tc*-$[Ru(OH_2)_2L_2][ClO_4]_2\cdot H_2O$ was prepared as before.[16b]

tc-*Dinitrobis*[2-(*phenylazo*)*pyridine*]*ruthenium*(II), *tc*-$[Ru(NO_2)_2(L^1)_2]$ (**2a**). A sample (0.36 g, 0.5 mmol) of *tc*-$[Ru(OH_2)_2(L^1)_2][ClO_4]_2\cdot H_2O$ was dissolved in acetonitrile (20 cm^3) and boiled for 15 min. The yellow-orange solution was cooled to room temperature. To this an aqueous solution of sodium nitrite (0.5 g) in water (30 cm^3) was added and the mixture was heated to reflux for 2 h. The solution gradually turned red. It was then concentrated to half its initial volume and kept overnight in a refrigerator. The dark crystals were collected by filtration, washed thoroughly with water, and finally dried *in vacuo* over P_4O_{10}. Yield 90% (Found: C, 47.20; H, 3.10; N, 20.30. Calc. for $C_{22}H_{18}N_8O_4Ru$: C, 47.20; H, 3.20; N, 20.05%); Λ_M(MeCN) 2.5 ohm^{-1} cm^2 mol^{-1}; $\nu_{max.}$(KBr) 1 360s (NO_2) and 1 370s cm^{-1} (N=N); $\lambda_{max.}$(CH_2Cl_2) 538, 455 (sh), 355 (sh), and 310 nm (ε 9 585, 3 355, 18 200, and 22 520 dm^3 mol^{-1} cm^{-1}).

The complexes *tc*-$[Ru(NO_2)_2(L^2)_2]$ (**2b**) and *tc*-$[Ru(NO_2)_2(L^3)_2]$ (**2c**) were prepared similarly using the appropriate *tc*-$[Ru(OH_2)_2L_2][ClO_4]_2\cdot H_2O$. Complex (**2b**), yield 85% (Found: C, 49.20; H, 3.90; N, 19.05. Calc. for $C_{24}H_{22}N_8O_4Ru$: C, 49.05; H, 3.75; N, 19.10%); Λ_M(MeCN) 1.0 ohm^{-1} cm^2 mol^{-1}; $\nu_{max.}$(KBr) 1 355s (NO_2) and 1 365s cm^{-1} (N=N); $\lambda_{max.}$(CH_2Cl_2) 540, 455(sh), 363, 310, and 290 (sh) nm (ε 9 420, 3 180, 17 820, 21 000, and 17 410 dm^3 mol^{-1} cm^{-1}). Complex (**2c**), yield 90% (Found: C, 49.30; H, 3.80; N, 19.15. Calc. for $C_{24}H_{22}N_8O_4Ru$: C, 49.05; H, 3.75; N, 19.10%); Λ_M(MeCN) 1.0 ohm^{-1} cm^2 mol^{-1}; $\nu_{max.}$(KBr) 1 355s (NO_2) and 1 365s cm^{-1} (N=N); $\lambda_{max.}$(CH_2Cl_2) 538, 455 (sh), 375, 315, and 290 (sh) nm (ε 9 080, 3 485, 22 860, 19 630, and 16 150 dm^3 mol^{-1} cm^{-1}).

tc-*Nitronitrosylbis*[2-(*phenylazo*)*pyridine*]*ruthenium*(II) *Perchlorate*, *tc*-$[\mathrm{Ru(NO)(NO_2)(L^1)_2}][\mathrm{ClO_4}]_2$ (**3a**).—A sample (0.11 g, 0.2 mmol) of *tc*-$[\mathrm{Ru(NO_2)_2(L^1)_2}]$ was treated with concentrated (10 mol $\mathrm{dm^{-3}}$) nitric acid (2 $\mathrm{cm^3}$) in a beaker placed in an ice-bath. The mixture was rubbed with a glass rod to make a paste. Ice-cold concentrated (10 mol $\mathrm{dm^{-3}}$) perchloric acid (2 $\mathrm{cm^3}$) was added dropwise with stirring. The mixture was then diluted to *ca.* 20 $\mathrm{cm^3}$ with ice-cold water. The orange crystals which separated were collected by filtration, washed with the minimum volume (*ca.* 2 $\mathrm{cm^3}$) of cold water, and dried *in vacuo* over $\mathrm{P_4O_{10}}$. Yield 90% (Found: C, 35.60; H, 2.60; N, 14.95. Calc. for $\mathrm{C_{22}H_{18}Cl_2N_8O_{11}Ru}$: C, 35.55; H, 2.40; N, 15.10%); Λ_M(MeCN) 265 $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$; $\nu_{max.}$(KBr) 1 950s (NO), 1 470 ($\mathrm{NO_2}$), and 1 380s $\mathrm{cm^{-1}}$ (N=N). Due to rapid conversion into the dinitro analogue, the solution spectrum could not be recorded.

The complexes *tc*-$[\mathrm{Ru(NO)(NO_2)(L^2)_2}][\mathrm{ClO_4}]_2$ (**3b**) and *tc*-$[\mathrm{Ru(NO)(NO_2)(L^3)_2}][\mathrm{ClO_4}]_2$ (**3c**) were prepared similarly using the same reactant stoicheiometry and conditions starting from the appropriate *tc*-$[\mathrm{Ru(NO_2)_2L_2}]$. Complex (**3b**), yield 90% (Found: C, 37.30; H, 2.65; N, 14.50. Calc. for $\mathrm{C_{24}H_{22}Cl_2N_8O_{11}Ru}$: C, 37.40; H, 2.85; N, 14.55%); Λ_M(MeCN) 280 $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$; $\nu_{max.}$(KBr) 1 950s (NO), 1 480 ($\mathrm{NO_2}$), and 1 375s $\mathrm{cm^{-1}}$ (N=N); $\lambda_{max.}$(MeCN) 410br and 340 nm (ε 9 830 and 12 150 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$). Complex (**3c**), yield 90% (Found: 37.70; H, 2.65; N, 14.45. Calc. for $\mathrm{C_{24}H_{22}Cl_2N_8O_{11}Ru}$: C, 37.40; H, 2.85; N, 14.55%); Λ_M(MeCN) 295 $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$; $\nu_{max.}$(KBr) 1 955s (NO), 1 455 ($\mathrm{NO_2}$), and 1 375 $\mathrm{cm^{-1}}$ (N=N); $\lambda_{max.}$(MeCN) 415br and 340 nm (ε 10 300 and 12 350 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$).

Conversion of tc-$[\mathrm{Ru(NO)(NO_2)(L^2)_2}][\mathrm{ClO_4}]_2$ (**3b**) *into tc*-$[\mathrm{Ru(NO_2)_2(L^2)_2}]$ (**2b**).—The compound (**3b**) (8.15 g, *ca* 0.2 mmol) was dissolved in water–acetonitrile (4:1, v/v; 30 $\mathrm{cm^3}$) and was stirred for 1 h at room temperature. Initially the solution was orange but in 0.5 h it became red. It was then concentrated under reduced pressure to half its initial volume. The dark crystals were collected by filtration and dried *in vacuo* over $\mathrm{P_4O_{10}}$. Yield 70%. Spectral data for the compound isolated correspond exactly to that of an analysed sample of (**2b**).

Conversion of tc-$[\mathrm{Ru(NO_2)_2(L^1)_2}]$ *into tc*-$[\mathrm{Ru(OH_2)_2(L^1)_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$.—A sample (0.14 g, 0.25 mmol) of *tc*-$[\mathrm{Ru(NO_2)_2(L^1)_2}]$ was suspended in 1 mol $\mathrm{dm^{-3}}$ aqueous perchloric acid (10 $\mathrm{cm^3}$) and the mixture heated to reflux for 3 h. The solution was then cooled to room temperature and filtered to remove insoluble residues. Crystals of sodium perchlorate (*ca.* 1 g) were then added with stirring. The mixture was kept overnight in a refrigerator. Dark needle-shaped crystals were collected by filtration, washed with the minimum volume (*ca.* 5 $\mathrm{cm^3}$) of cold water, and finally dried *in vacuo* over $\mathrm{P_4O_{10}}$. Yield 55%. Electronic spectral data for the compound isolated correspond exactly to those for a known,[16b] analysed sample of *tc*-$[\mathrm{Ru(OH_2)_2(L^1)_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$.

The same reaction was also carried out in 1 mol $\mathrm{dm^{-3}}$ aqueous sulphuric acid and the compounds were isolated by addition of saturated aqueous sodium perchlorate solution. The use of aqueous perchloric acid results in an isomerically purer product.

The complex *tc*-$[\mathrm{Ru(NO)(NO_2)(L^1)_2}][\mathrm{ClO_4}]_2$ was similarly converted into *tc*-$[\mathrm{Ru(OH_2)_2(L^1)_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$ using 1 mol $\mathrm{dm^{-3}}$ aqueous perchloric acid. Yield 65%.

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