Chemistry of Ruthenium. Part 8.[1] New Tris Complexes of Ruthenium(III). Synthesis, Spectra, and Redox Activity

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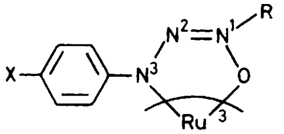
A group of new low-spin tris complexes of ruthenium(III) has been synthesized using triazene 1-oxides, RN(O)=N–NH–C_6H_4X-*p* (HL; R = Et or Ph, X = Me, H, Cl, CO_2Et, or NO_2) as ligands. The green to yellow-green complexes [RuL_3] are believed to have a meridional RuN_3O_3 co-ordination sphere. They display ligand ⟶ metal charge-transfer transitions in the region 550—750 nm. In acetonitrile solution the [RuL_3] complexes exhibit a quasi-reversible Ru^{III}–Ru^{II} couple (E_{298}^0, −0.6 to −1.2 V *vs.* s.c.e.) and a nearly reversible Ru^{IV}–Ru^{III} couple (E_{298}^0, 0.2—0.7 V *vs.* s.c.e.) at a platinum working electrode. The E_{298}^0 values of both couples correlate linearly with the Hammett constant of substituent X. The reaction constants lie in the range 0.1—0.2 V. The electronic spectra of [RuL_3]$^-$ and [RuL_3]$^+$ are briefly reported. The former complex is unstable.

The present work stems from our concurrent interest in new complexes of ruthenium [1,2] and in the metal-binding properties [3] of triazene 1-oxides, RN(O)=N–NH–C_6H_4X-*p* (HL; R = Et or Ph, X = Me, H, Cl, CO_2Et, or NO_2). Though the known chelate chemistry of triazene 1-oxides is considerable [4] and the neutral tris-chelates [ML_3] (M = Cr, Fe, Co, or Rh) are well documented,[5,6] nothing is reported about ruthenium triazene 1-oxides. Herein we describe the synthesis and characterization of a group of tris-chelates of trivalent ruthenium, [RuL_3] (1). The various ligands used (HL^1—HL^9) differ in the substituents R and X. Whereas well characterized complexes of ruthenium in the +2 and +3 states are common, this is not so for the +4 state.[7] Among tris-chelates the occurrence of both the ruthenium(III)–ruthenium(II) and ruthenium(IV)–ruthenium(III) couples are thus far documented in just two systems: β-diketonates [8] and dithiocarbamates.[9] Hence the electron-transfer properties of [RuL_3] are of considerable interest. Voltammetric examination of the triazene 1-oxide complexes has indeed revealed the presence of the Ru^{III}–Ru^{II} and Ru^{IV}–Ru^{III} couples. The effects of the substituents R and X on the formal potentials of these couples are compared.



	R	X		R	X
[RuL^1_3] (1a)	Et	Me	[RuL^6_3] (1f)	Ph	Me
[RuL^2_3] (1b)	Et	H	[RuL^7_3] (1g)	Ph	H
[RuL^3_3] (1c)	Et	Cl	[RuL^8_3] (1h)	Ph	Cl
[RuL^4_3] (1d)	Et	CO_2Et	[RuL^9_3] (1i)	Ph	CO_2Et
[RuL^5_3] (1e)	Et	NO_2			

Results and Discussion

Syntheses, Spectra, and Structures.—The reaction of the blue reduced solution [10] formed by boiling $RuCl_3·3H_2O$ in ethanol with the conjugate base (HL + K_2CO_3) of HL at room temperature in air yields [RuL_3] (analytical data in Table 1). The temperature during synthesis should not rise above 25 °C; otherwise, unidentified nitrosyl species contaminate the product. The green [(1a)—(1e)] to yellow-green [(1f)—(1i)] non-electrolytic crystalline complexes are soluble in common organic solvents. In two cases where magnetic moments were determined, namely (1g) and (1i), the moments are respectively 1.80 and 1.90 B.M. (1.67 and 1.76 × 10^{-23} A m^2) corresponding to low-spin ($S = \frac{1}{2}$) character. In contrast, [FeL_3] is high-spin.[3,6]

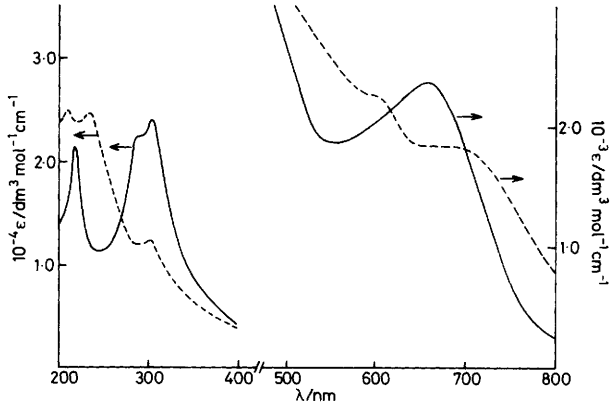


Figure 1. Electronic absorption spectra of [RuL^2_3] (——) and [RuL^8_3] (— — —) in acetonitrile solution

The chelating mode of triazene 1-oxides as depicted in (1) has been directly proved by *X*-ray diffraction work on nickel(II) [11] and cobalt(II) [12] complexes and by ^1H n.m.r. data for diamagnetic [5] tris complexes of cobalt(III) and rhodium(III). Among the vibration modes displayed by the triazene 1-oxide chelate ring, most characteristic [4] are those pertaining to the triazene moiety and the N ⟶ O fragment (Table 1).

The u.v.–visible spectral results (200—800 nm) for some [RuL_3] complexes in MeCN solution are in Table 1 and Figure 1. One or two allowed bands occur in the 550—750 nm region. These are assigned to L ⟶ Ru charge-transfer transitions as in the case [5,6] of [FeL_3] and [CoL_3].

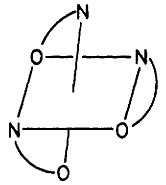
Since L is unsymmetrical, [RuL_3] can in principle occur as meridional and facial isomers. In the case of [CoL_3] and [RhL_3] only the sterically favourable meridional form occurs.[5] Chromatography of [RuL_3] preparations on silica gel and alumina columns failed to show the presence of isomers. We therefore assume that [RuL_3] also occurs exclusively in the meridional form (see below).

We note that well characterized tris-chelates of ruthenium(III) are relatively limited in number and are known primarily with the co-ordination spheres O_6,[13] S_6,[14] O_3S_3,[15] N_6,[16] and

Table 1. Microanalytical and spectroscopic data for the ruthenium(III) complexes

	Analysis [a] (%)			I.r.[b] (cm^{-1})		Electronic spectral data [c] λ/nm (ε/dm^3 mol^{-1} cm^{-1})			
Complex	C	H	N	ν(N_3)(triazene)	ν(NO)				
(1a)	50.7	5.7	19.3	1 480vs, 1 440s, 1 430m	1 260s	666	308 (sh)	272	216
	(51.0)	(5.7)	(19.8)			(2 100)	(14 000)	(15 500)	(21 000)
(1b)	48.1	5.1	21.0	1 480vs, 1 450br, 1 420w	1 265s	658	304	288	218
	(48.6)	(5.1)	(21.2)			(2 300)	(24 000)	(22 500)	(21 000)
(1c)	40.8	3.9	17.6	1 485vs, 1 450s, 1 430m	1 280s	660	306 (sh)	272	216
	(41.3)	(3.9)	(18.1)			(3 000)	(24 000)	(26 000)	(25 000)
(1d)	49.2	5.2	15.2	1 500s, 1 450br, 1 415w	1 270s	650	430 (sh)	328	284
	(48.9)	(5.2)	(15.6)			(2 700)	(8 300)	(25 500)	(23 000)
						242	214		
						(19 000)	(22 000)		
(1e)	39.2	3.6	22.8	1 490s, 1 450s, 1 420w	1 260s	666 (sh)	480 (sh)	363	274
	(39.6)	(3.7)	(23.1)			(2 400)	(6 200)	(59 000)	(16 500)
						240	216		
						(17 000)	(23 000)		
(1f)	60.7	4.8	15.7	1 500s, 1 480vs, 1 460m	1 275m	708 (sh)	600 (sh)	344	290
	(60.1)	(4.6)	(16.2)			(2 100)	(2 400)	(20 000)	(22 000)
						242	212		
						(27 000)	(27 000)		
(1g)	57.9	4.1	16.8	1 475vs, 1 450w, 1 365vs	1 250s	710 (sh)	590 (sh)	388 (sh)	340 (sh)
	(58.6)	(4.1)	(17.1)			(2 000)	(2 800)	(18 000)	(23 000)
						290	240		
						(26 000)	(32 000)		
(1h)	50.8	3.3	14.8	1 475vs, 1 440w, 1 370vs	1 250m	712(sh)	608 (sh)	304	236
	(51.4)	(3.2)	(15.0)			(1 800)	(2 200)	(12 000)	(25 000)
						210			
						(25 000)			
(1i)	56.2	4.3	13.4	1 480vs, 1 460s, 1 390vs	1 260s	712 (sh)	606	432 (sh)	358
	(56.7)	(4.4)	(13.2)			(2 000)	(3 100)	(18 500)	(33 000)
						318	252 (sh)	236	
						(31 000)	(31 000)	(33 000)	

[a] Calculated values are in parentheses. [b] KBr disc; vs = very strong, s = strong, br = broad, w = weak, m = medium. [c] In acetonitrile.



N_3S_3.[17] The RuN_3O_3 co-ordination sphere present in (1) is rare.[18]

Electron-transfer Properties.—The redox activity of [RuL_3] was studied in acetonitrile solution (0.1 mol dm^{-3} in tetraethylammonium perchlorate, 298 K) using cyclic and differential pulse voltammetry at a platinum working electrode. Results are collected in Table 2. All potentials are referred to a saturated calomel electrode (s.c.e.). Each complex undergoes a one-electron reduction and a one-electron oxidation in the potential ranges −0.6 to −1.2 V and 0.2 to 0.7 V respectively. Since free triazene 1-oxide ligands and their complexes with redox-inactive metal ions do not undergo[3] electron transfer in the above ranges, the reductive and oxidative responses of [RuL_3] are due to the metal ion.

Table 2. Cyclic and differential pulse voltammetric data [a] at 298 K in acetonitrile

	Ru^{III}–Ru^{II} couple		Ru^{IV}–Ru^{III} couple	
Complex	c.v.[b] $-E_{298}^0$/V (ΔE_p/mV)	d.p.v.[c] E_{298}^0/V	c.v.[b] E_{298}^0/V (ΔE_p/mV)	d.p.v.[c] E_{298}^0/V
(1a)	1.20 (180)	1.22	0.24 (60)	0.23
(1b)	1.16 (180)	1.18	0.28 (60)	0.27
(1c)	1.04 (110)	1.03	0.38 (60)	0.37
(1d)	0.92 (120)	*d*	0.49 (100)	*d*
(1e)	0.69 (60)	0.71	0.60 (80)	0.59
(1f)	0.83 (160)	0.84	0.45 (60)	0.45
(1g)	0.82 (160)	*d*	0.51 (70)	*d*
(1h)	0.70 (180)	0.72	0.58 (80)	0.57
(1i)	0.66 (180)	0.68	0.66 (90)	0.64

[a] Platinum electrode; supporting electrolyte [NEt_4][ClO_4] (0.1 mol dm^{-3}); all potentials are referenced to s.c.e. [b] $E_{298}^0 = 0.5(E_{pc} + E_{pa})$; E_{pc} and E_{pa} are cathodic and anodic peak potentials respectively; v = 100 mV s^{-1}. [c] Modulation amplitude (ΔE) is 25 mV; v = 10 mV s^{-1}; $E_{298}^0 = E_p + 0.5\Delta E$, where E_p is d.p.v. peak potential. [d] Not measured.

The Ruthenium(III)*–Ruthenium*(II) *Couple.*—In cyclic voltammetry (c.v.) at relatively slow scan rates (v = 20—50 mV s^{-1}) the reduction wave of [RuL_3] has the height required[3] for a one-electron transfer but on scan reversal the anodic response appears with diminished height, or is non-existent. On increasing the scan rate the anodic response becomes progressively more prominent (Figure 2). Thus the electrode reaction (1) is followed by the decomposition reaction (2).

$$[RuL_3] + e^- \longrightarrow [RuL_3]^- \qquad (1)$$

$$[RuL_3]^- \xrightarrow{k_f} \text{products} \qquad (2)$$

The triazene 1-oxide ligand is not well suited for the stabiliz-

Table 3. Coulometric oxidation and reduction of [RuL$_3$] and electronic spectra of [RuL$_3$]$^+$ and [RuL$_3$]$^-$ in acetonitrile [a]

	Coulometric data [b]				Electronic spectral data [c] λ/nm (ε/dm^3 mol^{-1} cm^{-1})						
Complex	Sample (mg)	Potential (V)	Q	n							
(a) Oxidation					(a) Oxidized species, [RuL$_3$]$^+$						
(1c)	7.50	+0.65	0.98	0.94	872 (4 500)	820 (sh) (4 200)	600 (3 700)	480 (sh) (3 500)	304 (sh) (23 500)	276 (23 000)	236 (sh) (26 000)
(1g)	5.75	+0.74	0.68	0.91	d						
(1h)	4.93	+0.82	0.52	0.91	d						
(1i)	4.87	+0.90	0.45	0.92	884 (4 500)	840 (sh) (4 200)	664 (sh) (3 000)	350 (32 000)	320 (sh) (29 500)	244 (32 000)	
(b) Reduction					(b) Reduced species, [e] [RuL$_3$]$^-$						
(1g)	7.80	−1.10	1.15	1.13	580, 346, 288, 240						
(1h)	4.93	−1.00	0.65	1.14	d						
(1i)	4.85	−0.94	0.56	1.14	608, 360, 252						

[a] Supporting electrolyte [NEt$_4$][ClO$_4$] (0.1 mol dm^{-3}). [b] Coulometric data are averages of at least three independent measurements; Q is the coulomb count at the end of exhaustive electrolysis; $n = Q/Q'$ where Q' is the calculated coulomb count for an 1e$^-$ transfer. [c] Spectral data are taken immediately after electrolysis. [d] Not measured. [e] Absorption coefficients are not calculated, as decomposition of [RuL$_3$]$^-$ occurs (see text).

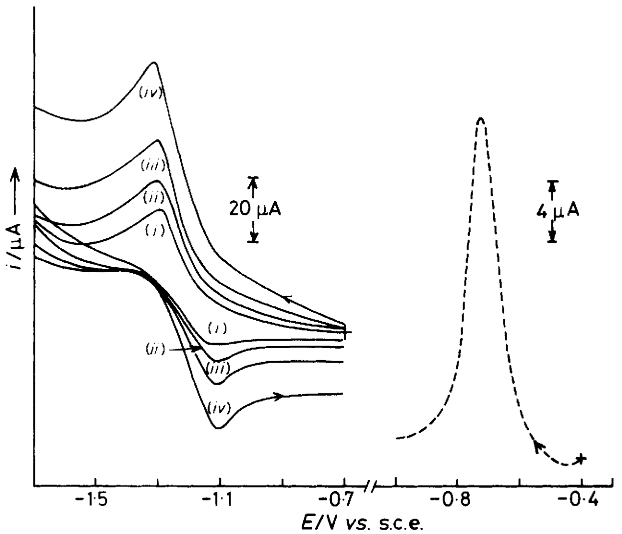


Figure 2. Cyclic voltammograms of [RuL$^1_3$] (——) (0.98 mol dm^{-3}) at scan rates (i) 50, (ii) 100, (iii) 200, and (iv) 500 mV s^{-1}; and d.p.v. of [RuL$^5_3$] (— — —) (0.82 mol dm^{-3}) at v = 10 mV s^{-1} and modulation amplitude 25 mV. In acetonitrile (0.1 mol dm^{-3} [NEt$_4$]-[ClO$_4$]) with a platinum working electrode

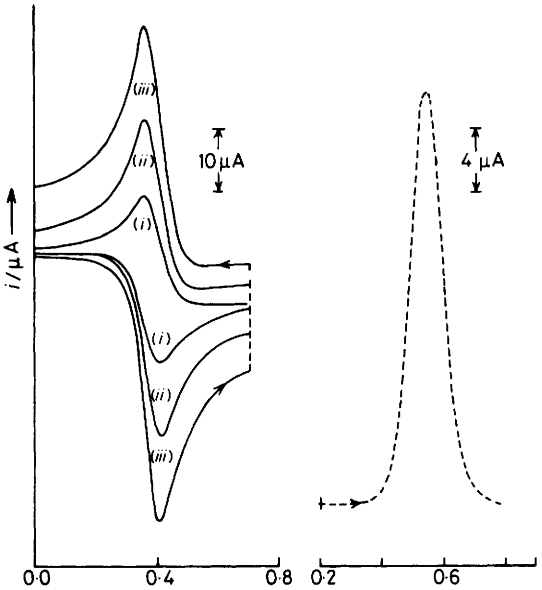


Figure 3. Cyclic voltammetric response of [RuL$^3_3$] (——) (0.66 mol dm^{-3}) at scan rates (i) 20, (ii) 50, and (iii) 100 mV s^{-1}; and d.p.v. of [RuL$^8_3$] (— — —) (1.48 mol dm^{-3}) at v = 10 mV s^{-1} and modulation amplitude 25 mV. In acetonitrile (0.1 mol dm^{-3} [NEt$_4$]-[ClO$_4$]) with a platinum working electrode

ation of the ruthenium(II) state. In the case of iron (and cobalt)[3] the reduced complex [ML$_3$]$^-$ is more stable than [RuL$_3$]$^-$ but still not stable enough for isolation.

At scan rates where both cathodic and anodic responses are observable, we can write the couple as equation (3). The peak-to-peak separations (ΔE_p) lie in the range 110—180 mV (v = 100 mV s^{-1}). The electron-transfer process is thus quasi-reversible. The formal potentials $E_{298}{}^0$, calculated as the average of the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials are in Table 2. Differential pulse voltammetric (d.p.v.) data are in full agreement with c.v. results (Figure 2 and Table 2). The $E_{298}{}^0$ of the couple in equation (3) is systematically more negative than that of the corresponding iron couple[3] (by *ca.* 400 mV). In dithiocarbamates a similar shift (*ca.* 300 mV) occurs.[8,9] In β-diketonates the shift is smaller (*ca.* 30 mV).[10,19]

$$[\mathrm{Ru^{III}L_3}] + e^- \rightleftharpoons [\mathrm{Ru^{II}L_3}]^- \qquad (3)$$

The one-electron nature of equation (3) was confirmed in several cases by coulometry at a potential *ca.* 200 mV more negative than E_{pc} (Table 3). The coulomb count rapidly reached the 1e$^-$ value and thereafter a slow count continued to accumulate. This may be due to the decomposition products of [RuL$_3$]$^-$. The coulometrically reduced solution is brown in colour. Several absorption bands are displayed by such solutions (Table 3). Since the solution also contains products of [RuL$_3$]$^-$ decomposition, the assignment and the absorption coefficient of the bands are not reported.

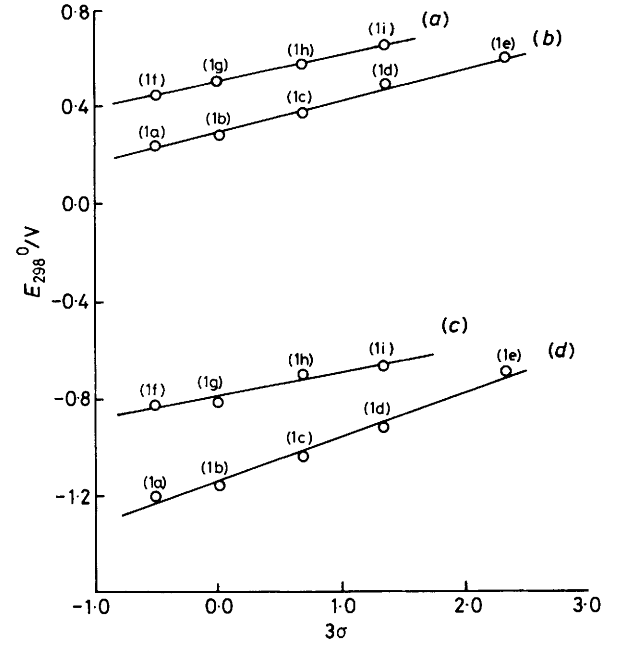


Figure 4. Least-squares plots of $E_{298}{}^0$ *versus* 3σ for ruthenium(IV)–ruthenium(III) couples [curves (*a*) and (*b*)] and ruthenium(III)–ruthenium(II) couples [curves (*c*) and (*d*)]; values of ρ are (*a*) 0.11, (*b*) 0.13, (*c*) 0.10, and (*d*) 0.18 V

The Ruthenium(IV)*–Ruthenium*(III) *Couple.*—The behaviour of this couple is much more predictable than that of equation (3). Here anodic and cathodic peak heights are equal. The heights increase as the square root of the scan rate (Figure 3). The peak-to-peak separation is 60 mV in a number of cases (Table 2) showing that the electrode process (4) is nearly

$$[Ru^{IV}L_3]^+ + e^- \rightleftharpoons [Ru^{III}L_3] \qquad (4)$$

reversible. The stereochemistries for $[RuL_3]$ and $[RuL_3]^+$ are thus likely to be grossly similar. In the case of tris-dithiocarbamates, solvent[20] or anion[21] association is known to give rise to seven-co-ordination when the metal atom is oxidized to the +4 state. Whether a similar situation occurs for $[RuL_3]^+$ is not known. Isolation of the $[RuL_3]^+$ species as salts in the crystalline state is a definite possibility. Cyclic voltammetric and d.p.v. $E_{298}{}^0$ values for equation (4) are in excellent agreement with each other.

The one-electron stoicheiometry of equation (4) is fully corroborated by constant-potential coulometry at a potential of *ca.* 200 mV more positive than E_{pa} (Table 3). The solution colour of $[RuL_3]^+$, like $[RuL_3]$, is green. The coulometrically oxidized solution is quite stable and displays several bands above 600 nm (Table 3). These bands are evidently of L $\longrightarrow$ Ru^{IV} origin. Significantly, the bands occur at energies lower than those of $[RuL_3]$.

Linear Free-energy Correlation.—The $E_{298}{}^0$ values of the couples of equations (3) and (4) depend on X. The values decrease with increase in electron-releasing power of the substituents for both couples. Here the appropriate Hammett free-energy relationship[3,22] is (5), where $\Delta E_{298}{}^0$ is the shift in

$$\Delta E_{298}{}^0 = 3\sigma\rho \qquad (5)$$

potential from the standard (X = H), 3σ is the total substituent constant for three X substituents of three ligands and ρ is the reaction constant. The $E_{298}{}^0$ *versus* 3σ plots are excellently linear for both couples (3) and (4). The observed ρ values (Figure 4) compare well with those of other $[ML_3]$ (M = Fe or Co) systems[3] which display only the metal(III)–metal(II) couple. Whereas a few cases of a linear correlation between $E_{298}{}^0$ and σ for the Ru^{III}–Ru^{II} couple are known,[8,23] the present work provides the first neat example of such correlation for the Ru^{IV}–Ru^{III} couple. In the case of tris-β-diketonates, substituent effects on this couple are small.[8]

For a given X, the complexes with R = Et have lower $E_{298}{}^0$ values than those of the complexes with R = Ph (Table 2). This is expected in view of the higher electron-releasing power of the Et group.

Conclusions

The range of the metal binding capacity of triazene 1-oxides is augmented by the synthesis of low-spin ruthenium tris-chelates, $[RuL_3]$, having the relatively rare RuN_3O_3 co-ordination sphere. Following the acetylacetonates and dithiocarbamates, $[RuL_3]$ constitutes the third group of tris-chelates in which both the ruthenium(III)–ruthenium(II) and ruthenium(IV)–ruthenium(III) couples are shown to occur. Systematic substituent effects on electrode potentials are revealed for both couples. The binding of triazene 1-oxides to the bis(2,2′-bipyridyl)ruthenium(II) and bis[2-(phenylazo)pyridine]ruthenium(II) fragments is under investigation.

Experimental

Chemicals and Starting Materials.—The triazene 1-oxides (HL^1—HL^9) were prepared as usual[5] and $RuCl_3 \cdot 3H_2O$ was purified as described previously.[1,2] Electrochemically pure acetonitrile and tetraethylammonium perchlorate were obtained as before.[1–3]

Measurements.—Solution electrical conductivity was measured in acetonitrile using a Philips PR 9500 bridge with a solute concentration of *ca.* 10^{-3} mol dm^{-3}. Electronic spectra and i.r. spectra (KBr disc, 4 000—400 cm^{-1}) were obtained using Pye Unicam SP8-150 and Beckman IR-20A spectrometers respectively. Magnetic susceptibility was measured on a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant. In general, electrochemical data were collected with the help of a PAR 370-4 electrochemistry system as described previously;[3] d.p.v. was carried out using a PAR M-174A polarographic analyzer. All experiments were performed under a dry and purified nitrogen atmosphere. Planar Beckman model 39273 platinum-inlay working electrode, platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (s.c.e.) were used in the three electrode measurements. The reference electrode (PAR model K0077) was connected with the electroactive solution through a fritted salt bridge filled with a 0.1 mol dm^{-3} solution of $[NEt_4][ClO_4]$ in acetonitrile–water (1 : 1). A platinum wire-gauge working electrode was used in coulometric experiments. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. The following σ values for *para* substituents were used:[3] Me, −0.17; H, 0.00; Cl, +0.23; CO_2Et, +0.45; NO_2, +0.78.

Syntheses of Compounds.—The compounds were prepared using similar methods. Details are therefore given for a representative complex.

Tris(1-*ethyl*-3-p-*tolyltriazene*-1-*oxidato*)*ruthenium*(III) (1a). Ruthenium trichloride trihydrate (260 mg, 1 mmol) was dissolved in ethanol (20 cm^3) and the solution was evaporated nearly to dryness on a water bath. The blue residue was dissolved in ethanol (20 cm^3) and the solution cooled to 0 °C (solution A). The ligand, 1-ethyl-3-*p*-tolyltriazene-1-oxide (540 mg, 3 mmol), was separately dissolved in ethanol (100 cm^3) and K_2CO_3 (300 mg, 2.2 mmol) was added. The mixture was heated on a water bath. The red solution (with residual K_2CO_3) thus obtained was cooled to 0 °C (solution B). Solution A was added dropwise to solution B over a period of 30 min under magnetic stirring. After 12 h, 6 cm^3 water was added dropwise to the reaction mixture and magnetic stirring was continued for a further 6 h. At this stage, the volume of the solution was *ca.* 10 cm^3 and a solid mass had separated. This mass was filtered off, thoroughly washed with cold water and then dried *in vacuo* over P_4O_{10}. It was dissolved in a small volume of benzene (*ca.* 10 cm^3). The solution was subjected to chromatography on a silica gel or neutral alumina column (30 × 2 cm) using benzene as eluant. A green band was eluted and a brown band remained at the top of the column. After removal of benzene from the eluant a green gummy mass was left which was dissolved in dichloromethane. On addition of hexane, crystals separated. These were collected by filtration and dried over P_4O_{10} *in vacuo* (yield *ca.* 40%).

Acknowledgements

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