1,10-Phenanthroline and 2,2′-Bipyridyl Complexes of Rhodium(III)

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The preparation of *cis*-$[Rh(aa)_2Cl_2]^+$ (aa = 2,2′-bipyridyl or 1,10-phenanthroline) has been re-examined and shown to be catalytic. The preparation and characterisation of *cis*-$[Rh(aa)_2X_2]^{n+}$ (X = I^-, CN^-, H_2O, and NH_3) and *cis*-$[Rh(aa)_2ClY]^{m+}$ (Y = H_2O, NH_3, pyridine, and NO_2^-) is described and the possible mechanisms of base hydrolysis and of substitution by cyanide and by iodide into *cis*-$[Rh(aa)_2Cl_2]^+$ are discussed; the effect of dioxygen on these substitutions is also discussed. The resolution of *cis*-$[M(aa)_2Cl_2]^+$ (M = Rh or Ir) into optical isomers is described and their stability is discussed. A convenient catalytic preparation of $[Rh(aa)_3]^{3+}$ is given.

BECAUSE of the catalytic formation of *trans*-$[Rh(py)_4Cl_2]^+$ and its unusual reactivity in the presence of reducing agents and/or absence of dioxygen,[1] we have extended these studies to $[Rh(aa)_2Cl_2]^+$ (aa = bipy or phen), which, although formally analogous to *trans*-$[Rh(py)_4Cl_2]^+$, has recently been shown to have a *cis*-configuration.[2-9] Most of this evidence for a *cis*-configuration of $[Rh(aa)_2X_2]^+$ is summarised in a recent review.[10] The reaction of rhodium trichloride with 2,2′-bipyridyl or 1,10-phenanthroline in the presence of reducing agents readily gives *cis*-$[Rh(aa)_2Cl_2]^+$.[11] These reactions were supposed to be catalytic but Rund[12] questioned this. As a result, we have re-examined this reaction and, because of the profound effect[1] of dioxygen on the formation and substitutions of *trans*-$[Rh(py)_4Cl_2]^+$, we have also studied the reactions in solutions containing rhodium trichloride and 2,2′-bipyridyl or 1,10-phenanthroline in the absence of both dioxygen and reducing agents.

Apart from *cis*-$[Rh(aa)_2X_2]^+$ (X = Cl,[11] Br,[2] or I[11]) and *cis*-$[Rh(phen)_2Cl(OH_2)]^{2+}$ which was reported only briefly[13] and not isolated from solution, no other bis(2,2′-bipyridyl)- or bis(1,10-phenanthroline)-rhodium(III) complexes have been described. In studying the behaviour of *cis*-$[Rh(aa)_2Cl_2]^+$ towards substitution, we have prepared *cis*-$[Rh(aa)_2X_2]^{n+}$ (X = I^-, CN^-, H_2O, and NH_3), *cis*-$[Rh(aa)_2ClY]^{m+}$ (Y = H_2O, NH_3, py, and NO_2^-) and $[Rh(aa)_3]^{3+}$. We have also resolved *cis*-$[M(aa)_2Cl_2]^+$ (M = Rh or Ir) into optical isomers using a chromatographic technique, and in some cases have studied their stability towards substitutions and reducing agents in an attempt to gain some insight into the substitution mechanisms.

Reaction of Rhodium Trichloride with 2,2′-*Bipyridyl or* 1,10-*Phenanthroline*.—The reaction of an aqueous solution of rhodium trichloride in hydrochloric acid (2M) with 1,10-phenanthroline or 2,2′-bipyridyl (3 mol) gives $(aaH)[Rh(aa)Cl_4]$.[9] In more dilute acid, partial hydrolysis occurs giving[9] $[Rh(aa)(H_2O)Cl_3]$, whilst in strong acid $(aaH)_2[Rh(H_2O)Cl_5]$ can[14] be obtained. When an aqueous solution of $(phenH)[Rh(phen)Cl_4]$ (1 mol) is boiled under reflux with phen (1 mol), a very slow reaction occurs giving[14] $[Rh(phen)_2Cl_2]^+$ after 20 h or $[Rh(phen)_3]^{3+}$ after 72 h. These reactions are greatly accelerated by the addition of two-electron reducing agents: † This effect was originally thought[11] to indicate catalysis by rhodium(I) or hydridorhodium(III) species in

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† Words meaning ' one-electron reductants ' or ' two-electron reducing agents ' would be useful: the old nomenclature ' monodelectronator, didelectronator, polydelectronator,' is not particularly euphonious, and describes oxidants only.

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the same way as does the formation of *trans*-$[Rh(py)_4Cl_2]^+$, which has recently been shown[1] to involve both these reduced species. However, Rund[12] suggested that the formation of *cis*-$[Rh(aa)_2Cl_2]^+$ from an aqueous ethanol solution of rhodium trichloride (1 mol) and ligand (2·2 mol) in the presence of hydrazinium monochloride N_2H_5Cl (*ca.* 0·3 mol) did not involve catalysis because of the presence of sufficient reducing agent to reduce all the rhodium to rhodium(I) which, he suggested, was oxidised to give the required rhodium(III) complex. We have shown this not to be the case since the above reaction, in the absence of ethanol and with only 0·02 mol of hydrazinium monochloride, gives *cis*-$[Rh(aa)_2Cl_2]^+$ in high yield at a comparable rate (see Experimental section).

The ratio of rhodium trichloride to ligand was found to be very important. Thus, using aqueous ethanol as solvent and hydrazinium monochloride (*ca.* 0·3 mol), with 2·0 mol of ligand we obtain an insoluble buff-coloured precipitate, shown by i.r. spectroscopy to be $[Rh(aa)_2Cl_2][Rh(aa)Cl_4]$, together with some *cis*-$[Rh(aa)_2Cl_2]Cl$. When using 3·3 mol of ligand, boiling for 5 min gives mainly *cis*-$[Rh(aa)_2Cl_2]^+$, whereas boiling for 30 min gives $[Rh(aa)_3]^{3+}$ in high yield. This reaction provides a convenient method for the preparation of the tris-complexes since previous recipes have involved[9,15] the reaction of rhodium trichloride with boiling ligand (*ca.* 270°).

The reaction of rhodium trichloride with hydrazinium monochloride in aqueous solution gives changes in the electronic spectra which suggest that rapid aquation occurs. Thus, treatment with hydrazinium monochloride (*ca.* 0·2 mol) at 30° gives a solution which shows absorption maxima at 450 and 350 nm suggesting[16] that the main product is *trans*-$[Rh(H_2O)_4Cl_2]^+$. (Heating this solution at 50° for 40 min produced no further change in $\lambda_{max.}$.) This aquation is similar to the results obtained by James *et al.* when using carbon monoxide[17] or ethylene[18] as catalysts. (That the latter reactions are not due to the removal of oxygen can readily be demonstrated by bubbling argon through an aqueous solution of rhodium trichloride when a solution with $\lambda_{max.}$ 475 and 377 nm is obtained, suggesting the presence of mainly $[Rh(H_2O)_3Cl_3]$.[16]) Addition of an ethanolic solution of ligand (2·2 mol) to this solution gives a good yield of *cis*-$[Rh(aa)_2Cl_2]^+$ and therefore *trans*-$[Rh(H_2O)_4Cl_2]^+$ must react with the ligand by preferential loss of water since it seems unlikely that, under the conditions of this experiment, complexes of the type *cis*-$[Rh(aa)_2Cl(H_2O)]^{2+}$ would react to give the dichloro-complex.

Finally, the reaction of rhodium trichloride with ligand (3·3 mol) in the absence of dioxygen has been studied. The reactants were dissolved in aqueous acetone and stirred at room temperature for 10 days. For 2,2′-bipyridyl, *cis*-$[Rh(bipy)_2Cl_2]^+$ and a moderate yield of $[Rh(bipy)_3]^{3+}$ were obtained, whereas for 1,10-phenanthroline, a 95% yield of *cis*-$[Rh(phen)_2Cl_2]^+$ was obtained. Substitutions with 1,10-phenanthroline, which is rigidly planar, are generally slower than those with the more flexible 2,2′-bipyridyl[19] and this could explain why $[Rh(phen)_3]^{3+}$ is not obtained in the above reaction. However, it is clear that these substitutions proceed much faster in the absence of dioxygen since the above reactions in the presence of dioxygen give no $[Rh(bipy)_3]^{3+}$ and only low yields of *cis*-$[Rh(aa)_2Cl_2]^+$. Thus rigorous exclusion of dioxygen, which can often be achieved by boiling solutions vigorously, is having a similar effect to that produced by the addition of two-electron reducing agents.

Preparation and Characterisation of Complexes of the Type cis-$[Rh(aa)_2X_2]^{n+}$ *and* cis-$[Rh(aa)_2ClY]^{m+}$.—X = Br^- *or* I^-. *cis*-$[Rh(aa)_2Br_2]^+$ Has previously been prepared from rhodium tribromide.[2] Both these complexes were well characterised.* *cis*-$[Rh(bipy)_2I_2]^+$ has been prepared by boiling an aqueous ethanolic solution of *cis*-$[Rh(bipy)_2Cl_2]^+$ with an excess of iodide in the presence of reducing agents:[11] indeed, boiling an aqueous ethanolic solution of *cis*-$[Rh(aa)_2Cl_2]^+$ with an excess of halide for 1 h provides the most convenient route for the preparation of all the complexes of the type *cis*-$[Rh(aa)_2X_2]^+$ (X = Br or I). The analytical and physical results for the dibromo-complexes are as previously described[2] and those obtained for the di-iodo-complexes are given in Tables 1 and 2.

Attempts to obtain rate constants by following the reaction (1) spectrophotometrically using dilute solutions

$$cis\text{-}[Rh(aa)_2Cl_2]^+ \underset{Cl^-}{\overset{I^-}{\rightleftharpoons}} cis\text{-}[Rh(aa)_2I_2]^+ \qquad (1)$$

(*ca.* 10^{-3}M[Rh]) gave irreproducible results and were noticeably affected by light. However, while working on a preparative scale, we found that the reaction of *cis*-$[Rh(aa)_2Cl_2]^+$ with iodide in aqueous ethanol is not accelerated by the addition of hydrazinium monochloride (0·02 mol) and replacement of ethanol by t-butanol or acetone has little effect on the rate of substitution. However, the di-iodo-complex could not be prepared by reaction (1) in aqueous solution, even in the presence of hydrazinium monochloride, because of

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* We wish to clarify an unnecessarily confused situation in the literature. Rhodium trichloride trihydrate in hot aqueous ethanol reacts with 1,10-phenanthroline, in the presence of an excess of potassium bromide, to give initially (phenH)[Rh(phen)Br_4] which on further heating is[4] partially converted to *cis*-$[Rh(phen)Br_2]Br$. When hydrazinium monochloride is used as catalyst the reaction gives[2,11] *cis*-$[Rh(phen)_2Br_2]Br$ rapidly and in high yield. The complexes *cis*-$[Rh(aa)_2Br_2]Br$ have been characterised[2] by means of electronic and vibrational spectra, *X*-ray powder photographs, and analytical data. The suggestion[20] that the dibromo-complex obtained[2] by Gillard and Heaton is really (phenH)[Rh(phen)Br_4] is simply not true.

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TABLE 1

Analytical and physical measurements for complexes of the type *cis*-$[Rh(aa)_2X_2]Z,xH_2O$ and *cis*-$[Rh(aa)_2ClY]Z,xH_2O$

						Found (%)			Required (%)		
aa	X	Y	Z	*x*	Λ †	C	H	N	C	H	N
Bipy	I		I	0	104	30·4	2·1	6·9	30·2	2·0	7·0
Phen	I		I	0	113	34·6	2·6	6·3	34·1	1·9	6·6
Phen	I		Cl	0		38·2	2·5	7·8	38·3	2·1	7·5
Bipy	H_2O		ClO_4	1	225 *	31·4	2·9	7·3	31·3	2·9	7·3
Phen	H_2O		ClO_4	2	201 *	34·7	3·1	6·6	34·6	2·9	6·7
Bipy		H_2O	ClO_4	1	154 *	34·7	3·4	8·0	35·0	2·9	8·2
Phen		H_2O	ClO_4	1	153 *	39·5	2·9	7·6	39·3	2·7	7·6
Bipy	CN		Cl	4	75	46·2	3·2	14·8	46·1	4·2	14·7
Bipy	CN		ClO_4	1		45·7	2·7	14·5	45·2	3·1	14·4
Phen	CN		Cl	2·5	81	52·6	3·3	14·1	52·4	3·5	14·1
Phen	CN		ClO_4	1		49·1	2·6	13·1	49·4	2·8	13·3
Phen		CN	Cl	1		51·6	3·1	12·1	51·9	2·8	12·6
Bipy		NH_3	ClO_4	2	196	33·9	2·8	9·8	34·2	3·3	10·0
Phen		NH_3	ClO_4	1	230	39·4	3·1	9·4	39·4	2·9	9·6
Phen	NH_3		ClO_4	3	293	33·9	2·9	9·7	33·9	3·3	9·9
Bipy		NO_2	Cl	2	85	41·9	3·3	12·2	42·2	3·5	12·3
Phen		NO_2	Cl	1·5	99	47·4	2·9	11·6	47·4	3·1	11·5
Phen		NO_2	ClO_4	1		43·8	2·8	10·6	43·5	2·7	10·6
Bipy		py	ClO_4	0	194	40·9	3·4	9·4	41·2	2·9	9·6
Phen		py	ClO_4	1	230	44·0	3·0	9·0	43·8	2·9	8·8 ‡

‡ Found Cl, 12·7 required Cl, 13·4%. † Conductivity (Ω^{-1} cm^2 mol^{-1}) of *ca.* 10^{-3} M-aqueous solutions or * nitromethane solutions.

TABLE 2

Visible and ultraviolet absorption spectra for rhodium(III) complexes with 2,2′-bipyridyl or 1,10-phenanthroline in aqueous solution: $\lambda_{max.}$ (nm) and ε (cm^{-1} l mol^{-1})

cis-$[Rh(phen)_2I_2]I$	408 (1300)	354 (3680)	335sh (4500)	322sh	300sh		274 (58,500)	220 (80,000)
cis-$[Rh(phen)_2(H_2O)_2](ClO_4)_3,2H_2O$ [a]		350 (1850)	334 (2320)	317sh	301 (14,500)	279sh (54,600)	273 (57,300)	224 (61,000)
cis-$[Rh(phen)_2(H_2O)Cl](ClO_4)_2,H_2O$ [a]		350 (2220)	334 (2530)	318sh	302sh (20,500)	281sh (46,200)	273 (53,600)	225sh (53,300)
cis-$[Rh(phen)_2(CN)_2]Cl,2{\cdot}5H_2O$		348 (1970)	332 (2340)	315sh	300 (19,200)	276sh (68,800)	272 (69,800)	223 (67,300)
cis-$[Rh(phen)_2(NH_3)Cl](ClO_4)_2,H_2O$		350 (2360)	334 (2560)	320sh	301sh (16,000)		273 (59,000)	226 (54,500)
cis-$[Rh(phen)_2(NH_3)_2](ClO_4)_3,3H_2O$		349 (1890)	333 (2260)	315sh	301 (14,400)	280sh (52,000)	272 (56,500)	223 (60,300)
cis-$[Rh(phen)_2(NO_2)Cl]Cl,1{\cdot}5H_2O$		349 (2070)	333 (2550)	319sh	300 (14,900)	278sh (48,000)	272 (53,100)	225sh (58,000)
cis-$[Rh(phen)_2(py)Cl](ClO_4)_2,H_2O$		352 (2660)	335 (3040)	320sh	303sh (15,000)		273 (56,000)	225sh (57,000)
$(H_3O)[Rh(phen)Cl_4],4H_2O$	449 (171)	356 (1540)	338 (1710)		297sh		272 (27,200)	220sh (80,000)
cis-$[Rh(bipy)_2I_2]I$		406 (1380)	313 (24,200)	303 (22,400)			238 (61,000)	
cis-$[Rh(bipy)_2(H_2O)_2](ClO_4)_3,H_2O$ [a]		350sh (89)	318 (24,700)	305 (25,000)	295sh	243 (25,200)	211 (46,000)	
cis-$[Rh(bipy)_2(H_2O)Cl](ClO_4)_2,H_2O$		350sh (180)	316 (24,200)	306 (28,900)		246 (27,600)	216 (51,000)	
cis-$[Rh(bipy)_2(CN)_2]Cl,4H_2O$		350sh (12)	314 (32,500)	302 (29,000)	293sh	241 (30,000)	209 (55,000)	
cis-$[Rh(bipy)_2(NH_3)Cl](ClO_4)_2,2H_2O$		350sh (150)	316sh (22,000)	306 (26,800)	298sh	246 (25,800)	212 (48,000)	
cis-$[Rh(bipy)_2(NO_2)Cl]Cl,2H_2O$		350sh (220)	316 (21,900)	305 (24,500)	296sh	240sh (28,100)	212 (57,600)	
cis-$[Rh(bipy)_2(py)Cl](ClO_4)_2$		350sh (230)	317 (24,100)	306 (26,700)	296sh	246 (27,200)	212 (66,000)	
$(H_3O)[Rh(bipy)Cl_4]$		446 (153)	350sh (930)	312 (13,300)	301 (9750)	263sh (11,500)	220 (36,000)	

[a] pH of these solutions was adjusted to *ca.* 1 with $HClO_4$.

the precipitation of a very insoluble yellow compound (identified as *cis*-$[Rh(aa)_2Cl_2]I$) which prevents further reaction. On addition of ethanol, t-butanol or acetone, this precipitate dissolves and the reaction proceeds.

$X = Y = H_2O$ *or* OH^-. Irradiation of aqueous solutions of *cis*-$[Rh(phen)_2Cl_2]^+$ has been briefly reported[13] to give *cis*-$[Rh(phen)_2Cl(OH_2)]^{2+}$: this is the only claim for an aquo-bis(2,2′-bipyridyl)- or bis-(1,10-phenanthroline)-rhodium(III) complex. However, we find that irradiation of aqueous solutions of *cis*-$[Rh(aa)_2Cl_2]^+$ (10^{-4}M) with a xenon lamp for 20 min gives (mainly) *cis*-$[Rh(aa)_2(OH_2)_2]^{3+}$ whereas Schwab and Rund[7] have claimed that irradiation of aqueous solutions of *cis*-$[Rh(phen)_2Cl_2]^+$ at specific wavelengths does not result in aquation. Hence the conditions of the experiment would appear to be very important in determining the course of the reaction and as a result more reliable preparative methods have been developed.

Basolo *et al.*[21] found that base hydrolysis of *cis*-$[Rh(aa)_2Cl_2]^+$, unlike that of *cis*-$[Rh(en)_2Cl_2]^+$,[22] was very slow at 80°. We find similar results at 90° but addition of ethanol or hydrazinium monochloride (0·02 mol) to this solution results in rapid (*ca.* 10 min) aquation and formation of the dihydroxy-complex which can be isolated from acidified solutions as *cis*-$[Rh(aa)_2(OH_2)_2]^{3+}$ in high yield. *cis*-$[Rh(aa)_2Cl(OH_2)]^{2+}$ results from boiling vigorously an aqueous solution of *cis*-$[Rh(aa)_2Cl_2]^+$ with sodium hydroxide (*ca.* 0·1M) for 2 min, followed by recrystallisation from acidic solutions; boiling vigorously for 5 min or more results in complete conversion to the dihydroxy-complex. The analytical and physical measurements are shown in Tables 1 and 2.

The electronic spectra of all the aquo-complexes show reversible changes with pH (see Table 3), whereas the spectra of *cis*-$[Rh(aa)_2X_2]^{n+}$ and *cis*-$[Rh(aa)_2ClY]^{m+}$ ($X = Y \neq OH_2$ or OH^-) are not affected by pH. In the case of *cis*-$[Rh(bipy)_2(OH_2)_2]^{3+}$, this change is rather large and occurs in the region of the first ligand band (*ca.* 310 nm). It was originally suspected that behaviour of this kind in complexes of heterocyclic nitrogen ligands might be due to covalent hydration of the ligand[2] but this has now been shown by n.m.r. measurements not to be a major effect in the present case.

TABLE 3

Variation in relative intensities and values of $\lambda_{max.}$ with pH for complexes of the type *cis*-$[Rh(aa)_2ClY]^{m+}$ and *cis*-$[Rh(aa)X_2]^{m+}$ ($X = Y = OH_2$ or OH)

aa	X or Y [a]	pH	$\lambda_{max.}$ (nm) [b]			
Bipy	X	1		317(1·00)	305(1·04)	242(1·33)
	X	7		312(1·00)	303(1·02)	245(1·02)
	X	13		311(1·00)	300(1·00)	250(0·96)
Bipy	Y	1		317(1·00)	307(1·22)	246(1·14)
	Y	7		317sh(1·00)	306(1·25)	247(1·16)
	Y	13		312(1·00)	303(0·92)	250(0·86)
Phen	X	1	349(0·05)	333(0·06)	301(0·27)	272(1·00)
	X	13	355(0·07)	335sh(0·08)	300sh(0·31)	272(1·00)
Phen	Y	1	350(0·06)	335(0·06)	303sh(0·27)	273(1·00)
	Y	13	354(0·07)	335(0·07)	298sh(0·33)	273(1·00)

[a] See heading to Table 3. [b] Figures in brackets are relative intensities.

The ^1H n.m.r. spectra of 2,2′-bipyridyl, $[M(bipy)_3]^{n+}$, and *cis*-$[Ir(bipy)_2Cl_2]^+$ have previously been studied and reliable assignments have been made.[3,23-25] Thus, for complexes of the type $[M(bipy)_3]^{n+}$, H^6 and $H^{6\prime}$ are equivalent and their resonance occurs at higher field than in the free ligand, whereas the other protons resonate at lower field than in the free ligand. This is to be contrasted with the spectra of complexes of the type *cis*-$[M(bipy)_2X_2]^{n+}$. In this case, H^6 and $H^{6\prime}$ are now inequivalent and their resonances are widely separated: one occurs in the same region as found for the tris-complex and can thus be assigned to $H^{6\prime}$ (see Figure 1) whereas the resonance due to H^6 occurs at lower field.

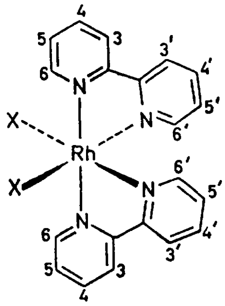

FIGURE 1 The numbering scheme employed in the text in commenting on the magnetic resonance of the complexes *cis*-$[Rh(bipy)_2X_2]^+$

Our assignments of the 220 MHz n.m.r. spectra of *cis*-$[Rh(bipy)_2(OH_2)_2]^{3+}$ in acid solution (pD1) and basic solution (pD9) (when the complex must exist as *cis*-$[Rh(bipy)_2(OH)_2]^+$ since no further change in electronic spectrum occurs pD9—13) are shown in Table 4. They have been deduced by comparison with the spectrum of *cis*-$[Ir(bipy)_2Cl_2]^+$, which was assigned[3] on the basis of spin-decoupling experiments, and also by comparison of the coupling constants with those observed in the free ligand.

The n.m.r. spectra clearly show that the complexes have the *cis*-configuration. All the peaks shift to higher field with increasing pH but no major shifts occur and no new peaks appear, thus providing no evidence for covalent hydration. By comparing the electronic spectra of *cis*-$[Rh(bipy)_2Cl_2]^+$, *cis*-$[Rh(bipy)_2(NH_3)Cl]^{2+}$, and $[Rh(bipy)_3]^{3+}$ ($\lambda_{max.}$ 311, 302sh; 316, 306; 318, 305 nm respectively), it seems probable that the difference between the electronic spectra of *cis*-$[Rh(bipy)_2(OH)_2]^+$, and *cis*-$[Rh(bipy)_2(OH_2)_2]^{3+}$ ($\lambda_{max.}$ 311, 300; 317, 305 nm respectively) is related to the change of total charge on the complex.

$X = Y = CN^-$. The reaction of *cis*-$[Rh(phen)_2Cl_2]^+$

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with an excess of sodium cyanide in aqueous solution at 90° for 1 h gives a pale yellow complex which has been shown to be mainly *cis*-$[Rh(phen)_2(CN)Cl]^+$, whereas boiling this solution vigorously for a few minutes or addition of hydrazinium monochloride to the solution at 90° and allowing reaction to proceed for *ca.* 10 min results in complete conversion to *cis*-$[Rh(phen)_2(CN)_2]^+$. *cis*-$[Rh(bipy)_2(CN)_2]^+$ has been prepared using similar procedures. The analytical and physical results are in Tables 1 and 2. The i.r. spectra of *cis*-$[Rh(phen)_2(CN)_2]^+$ and *cis*-$[Rh(bipy)_2(CN)_2]^+$ which were isolated as their chloride salts after ion-exchange showed clearly the presence of 2 sharp bands due to ν(C≡N) at 2147, 2141 and 2153, 2141 cm^{-1} respectively: the remainders of the spectra were virtually identical to those of the respective dichloro-analogues.

TABLE 4

^{1}H N.m.r. chemical shifts (τ) and coupling constants (Hz) for *cis*-bis(2,2′-bipyridyl) complexes at 220 and 100 MHz

Compound	H^3	$H^{3'}$	H^4	$H^{4'}$	H^5	$H^{5'}$	H^6	$H^{6'}$	J_{34}	$J_{3'4'}$	J_{45}	$J_{4'5'}$	J_{56}	$J_{5'6'}$
cis-$[Rh(bipy)_2(OH_2)_2]^{3+}$	1·10d	1·29d	1·24dd	1·62dd	1·70dd	2·38dd	0·59d	2·25d	8·0	8·0	8·0	8·0	6·0	6·0 [b]
cis-$[Rh(bipy)_2(OH)_2]^+$ [c]	1·30d	1·46d	1·48dd	1·82dd	1·91dd	2·57dd	0·73d	2·29d	8·0	8·0	8·0	8·0	5·5	5·5 [b]
cis-$[Ir(bipy)_2Cl_2]^+$	1·09	1·18	1·50	1·80	1·85	2·49	0·35	2·15	8·0	8·0	8·0	8·0	5·0	5·0 [d]

[a] *cis*-$[Rh(bipy)_2(OH_2)_2](ClO_4)_3$ in D_2O, adjusted to pD *ca.* 1 with $HClO_4$. [b] 220 MHz n.m.r. spectrum $J_{35} = J_{46} = 0$ Hz *cf.* ref. 3. [c] *cis*-$[Rh(bipy)_2(OH)_2](OH)$ in D_2O, adjusted to pD *ca.* 9 with NaOD. [d] 100 MHz n.m.r. spectrum in D_2O, ref. 3. d = doublet.

X = Y = NH_3. The reaction of *cis*-$[Rh(aa)_2Cl_2]^+$ with a vigorously boiling aqueous solution of ammonia gives *cis*-$[Rh(aa)_2(NH_3)Cl]^{2+}$ which has been isolated as the perchlorate salt as pale yellow crystals. Addition of hydrazinium monochloride (0·02 mol) to the above solution results in the rapid formation of the colourless *cis*-$[Rh(aa)_2(NH_3)_2]^{3+}$ complex (see Tables 1 and 2). The far-i.r. spectrum of *cis*-$[Rh(phen)_2(NH_3)Cl](ClO_4)_2$ shows a medium intensity band at 356 cm^{-1} which we tentatively assign to ν(Rh–Cl) since only weak bands occur in this region in the case of *cis*-$[Rh(phen)_2(NH_3)_2](ClO_4)_3$.

Y = py *or* NO_2^-. The reaction of *cis*-$[Rh(aa)_2Cl_2]^+$ with a vigorously boiling aqueous solution containing pyridine or sodium nitrite for 5 min gives *cis*-$[Rh(aa)_2(py)Cl]^{2+}$ or *cis*-$[Rh(aa)_2(NO_2)Cl]^+$ respectively (see Tables 1 and 2). The same complexes are obtained after addition of ethanol or hydrazinium monohydrochloride to this solution and no evidence was obtained for the formation of *cis*-$[Rh(aa)_2X_2]^{m+}$ (X = py or NO_2^-). The i.r. spectra of *cis*-$[Rh(aa)_2(NO_2)Cl]^+$ show absorptions at 1410, 1315, and 820 cm^{-1} which indicate [26] that these complexes contain the nitro ($-NO_2$) rather than the nitrito (–ONO) group.

Resolution of cis-$[M(aa)_2Cl_2]^+$ (M = Rh *or* Ir) *into Optical Isomers.*—Previous attempts to obtain a partial resolution of complexes of the type *cis*-$[M(aa)_2Cl_2]^+$ (M = Rh or Ir), using conventional techniques, proved unsuccessful.[2] A report by Broomhead and Grumley [27] claiming the resolution of *cis*-$[Ir(phen)_2Cl_2]^+$ has since been retracted but during the course of this work two reports of the resolution of *cis*-$[Rh(phen)_2Cl_2]^+$ have appeared.[7,8] We now report the resolution of *cis*-$[M(aa)_2Cl_2]^+$ (M = Rh or Ir) using a chromatographic technique and also comment upon the stability of these optical isomers. This chromatographic resolution technique has also proved to be useful for complexes containing ligands with the N–H grouping but, so far, we have been unable to resolve $[Rh(aa)_3]^{3+}$ by this method.

The c.d. spectra of the resolved complexes *cis*-$[M(aa)_2Cl_2]^+$ (M = Rh or Ir) are shown in Figures 2 and 3 (in each case the spectrum shown is that of the first band off the column). The dominant features of the c.d. spectra are the strong peaks which occur at frequencies corresponding to the first π–π* transitions of the ligands and are quite typical of metal complexes containing these ligands. The value of Δε (+94 l mol^{-1} cm^{-1}) at 279 nm obtained for *cis*-$[Rh(phen)_2Cl_2]^+$ compares favourably with the values obtained for complexes of the type *cis*-$[Ru(phen)_2(py)X]^+$ (Δε *ca.* 100 l mol^{-1} cm^{-1}; X = Cl, Br, I, *etc.*) [28] and suggests that chromatographic resolution of *cis*-$[Rh(phen)_2Cl_2]^+$ results in a fairly high degree of optical purity. Furthermore, the first few fractions off the column, when evaporated (at 20° in the dark) and passed down the column again, gave no detectable increase in activity. Unfortunately, it was impossible to make a similar comparison for *cis*-$[M(bipy)_2Cl_2]^+$ since there have been no other c.d.

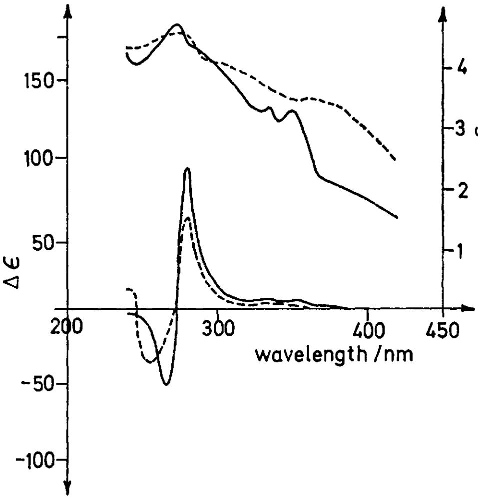

FIGURE 2 The absorption spectra (upper curves) and circular dichroism spectra (lower curves) of $[Rh(phen)_2Cl_2]^+$ (——) and of $[Ir(phen)_2Cl_2]^+$ (– – – –)

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[26] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 1963, p. 151.

[27] J. A. Broomhead and W. R. Grumley, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2126.

[28] B. Bosnich, *Inorg. Chem.*, 1968, **7**, 178.

spectra of monomeric *cis*-bis(2,2′-bipyridyl) complexes reported. The first fractions of *cis*-$[M(aa)_2Cl_2]^+$ to be eluted from the column all give c.d. spectra which show that the sign of the lowest exciton band is positive. This suggests that all four complexes have the same absolute configuration and comparison with the c.d. spectra [28] of $[Ru(phen)_2(py)X]^+$ suggests that the configuration is D [29] or $R(C_2)$.

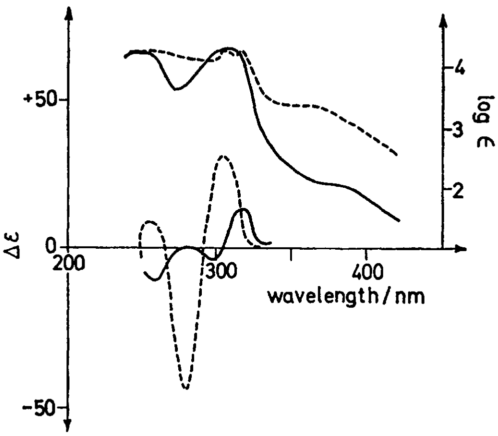

FIGURE 3 The absorption spectra (upper curves) and circular dichroism spectra (lower curves) of $[Rh(bipy)_2Cl_2]^+$ (——) and of $[Ir(bipy)_2Cl_2]^+$ (- - - -)

TABLE 5

Reactions of optically active $[Rh(phen)_2Cl_2]Cl$

Expt.[a] number	Reaction conditions	$T/°$	Time	$A/\%$ [b]
1	Heated in the dark	90	24 h	90
2	Boiled vigorously	100	1 min	37
3	Heated with a large excess of ethanol	80	90 min	85
4	Heated with a large excess of ethanol	80	24 h	0
5	Boiled vigorously with a large excess of NH_2NH_3Cl	100	1 min	35
6	Heated with sodium hydroxide, *ca.* 0·1M	90	5 min	90
7	Heated with sodium hydroxide, *ca.* 0·1M and an excess of NH_2NH_3Cl	90	5 min	46
8	Boiled vigorously with sodium hydroxide, *ca.* 0·1M	100	1 min	10 [c]
9	Boiled vigorously with sodium hydroxide, *ca.* 0·1M and an excess of ethanol	*ca.* 90	1 min	12 [c]
10	Product from expt. 9 brought to pH 7 with dilute HCl, treated with an excess of NaCl, and boiled vigorously	*ca.* 90	1 min	0 [d]
11	Rigorously degassed and heated with sodium hydroxide, *ca.* 0·1M	90	5 min	0 [c]
12	Rigorously degassed and allowed to stand in daylight	20	2 weeks	0
13	Rigorously degassed and allowed to stand in the dark	20	2 weeks	75
14	Allowed to stand in daylight, in air	20	2 weeks	20
15	Allowed to stand in the dark, in air	20	2 weeks	100
16	Irradiated with xenon lamp (solution $1{\cdot}0 \times 10^{-4}$M in complex, path length 1 cm)	20	5 min	30
17	As expt. 16	20	20 min	0
18	Boiled vigorously, with an excess of NaCN	100	2 min	98 [e]
19	Heated with an excess of NaI and ethanol	80	30 min	50 [f]

[a] In each experiment a portion of the stock solution (A = 100%) which contained resolved *cis*-$[Rh(phen)_2Cl_2]^+$ (*ca.* 10^{-3}M) and sodium chloride (*ca.* 10^{-2}M) was reacted as described. [b] A (expressed as %) is the optical activity remaining after reaction. [c-f] These products were identified as [c] *cis*-$[Rh(phen)_2(H_2O)Cl]^{2+}$; [d] *cis*-$[Rh(phen)_2Cl_2]^+$; [e] *cis*-$[Rh(phen)_2(CN)_2]^+$; [f] *cis*-$[Rh(phen)_2I_2]^+$.

Mechanism of Substitution in cis-$[Rh(phen)_2Cl_2]^+$. It has been shown earlier that substitution of chloride in *cis*-$[Rh(aa)_2Cl_2]^+$ by iodide is not catalysed by reducing agents whereas catalysis does occur with cyanide, hydroxide, ammonia, and pyridine substitution. In an attempt to gain further insight into these substitution mechanisms we have studied the stability of solutions containing optically active *cis*-$[Rh(phen)_2Cl_2]^+$ towards iodide, cyanide, and hydroxide and also towards heat, light, dioxygen and reducing agents. The experiments, which are summarised in Table 5 indicate that the resolved complex is very optically stable in the dark (1, 13, 15) * but loses activity rapidly if the solution is boiled vigorously (2), or irradiated with an intense light source (16, 17). The presence of dioxygen appears to inhibit the loss of optical activity both in the presence and absence of light (12—15). Base hydrolysis occurs with loss of activity (6—11) whereas cyanide and iodide substitution proceed with a high degree of retention of activity (18, 19). Base hydrolysis appears to be inhibited by dioxygen (6). The inhibition is removed by rigorous degassing (11), or partially removed by vigorous boiling (8), or addition of a reducing agent (7, 9). This type of behaviour towards dioxygen and reducing agents is very similar to that observed in halide substitution of *trans*-$[Rh(py)_4Cl_2]^+$, which has been shown to involve *trans*-$[Rh(py)_4]^+$ as the active catalyst,[1] and suggests that base hydrolysis of *cis*-$[Rh(phen)_2Cl_2]^+$ is also catalysed by a rhodium(I) intermediate, $[Rh(phen)_2]^+$. There has been a previous claim [30] for the preparation of the related complex, $[Rh(bipy)_2]^+$, and, although no structural information is yet available, it might reasonably be expected to have a similar structure to that of the isoelectronic complex $[Pd(bipy)_2]^{2+}$ which has a slightly distorted square-planar structure.[31] The involvement of a square-planar $[Rh(phen)_2]^+$ intermediate in the base hydrolysis of *cis*-$[Rh(phen)_2Cl_2]^+$ would thus explain the

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* Numbers in brackets refer to the experiment number in Table 5.

[29] R. D. Gillard, *Chem. in Britain*, 1967, **3**, 205.

[30] B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nuclear Chem.*, 1961, **23**, 207.

[31] M. Hinamoto, S. Ooi, and H. Kuroya, *Chem. Comm.*, 1972, 356.

catalysis and racemisation observed.* However, a square-planar rhodium(I) intermediate is clearly not responsible for the reaction of cyanide with *cis*-$[Rh(phen)_2Cl_2]^+$ since, although the reaction is catalysed by reducing agents, substitution occurs with a high degree of retention of optical activity. In order to explain the catalysis, it seems probable that a rhodium(I) intermediate is again involved but in this case, because of the presence of the highly polarisable nucleophile, cyanide, a five-co-ordinate species, $[Rh(phen)_2(CN)]$ is formed in which the phenanthroline ligands must still retain a *cis*-configuration. This five-co-ordinate intermediate can then undergo electron-transfer reactions with *cis*-$[Rh(phen)_2Cl_2]^+$ without racemisation. Iodide substitution in *cis*-$[Rh(phen)_2Cl_2]^+$, under the present conditions, is not catalysed and proceeds with retention of optical activity. The absence of catalysis may be attributed to pH effects since, in this case, the reaction was carried out at pH 7 whereas in all the other substitutions, where catalysis was found to occur, the solution always had pH $\geqslant 9$. It is now well known that catalysis of halide interchange in *trans*-$[Rh(py)_4Cl_2]^+$ and *trans*-$[Rh(en)_2Cl_2]^+$ is due to the presence of rhodium(I) which is in equilibrium with a rhodium(III) hydride. The concentration of rhodium(I) is increased by increasing pH and it would appear, in the case of *cis*-$[Rh(phen)_2Cl_2]^+$, that at pH *ca.* 7 the concentration of rhodium(I) is insufficient to induce catalysis.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Varian spectrometer at 220 MHz. I.r. spectra were measured as Nujol mulls on Perkin-Elmer 457 and 225 grating spectrometers. U.v. and visible spectra were recorded on a Unicam SP 800 spectrometer using matched silica cells. C.d. measurements were made on a Roussel-Jouan Dichrographe model 1B, with a sensitivity of $1{\cdot}5 \times 10^{-4}$/mm. Conductivities were determined on a Phillips PR 9500 conductivity bridge with a dipping cell. Resolution of complexes into chiroptical isomers was achieved by a chromatographic method similar to that described by Legg and Douglas.[33] The complex (0·1 g) was loaded onto a column containing Whatman CM32 cation exchange resin, then eluted (using a peristaltic pump) with 0·01M sodium chloride solution. The flow rate was 1 ml min^{-1}. Microanalyses were carried out by Mr. G. Powell of this laboratory.

Reaction of Rhodium Trichloride with Bipy or Phen.—1. *Using Hydrazinium Monochloride as Catalyst.* Rhodium trichloride (0·263 g; 1×10^{-3} mol) and phen (0·44 g; $2{\cdot}2 \times 10^{-3}$ mol) were dissolved in hot water. Boiling this solution for 10 min gave an orange solution with $\lambda_{max.}$ 422 nm which suggested the formation of $[Rh(phen)Cl_4]^-$.[9] Boiling for a further 10 min produced no further change in the electronic spectrum. However, addition of hydrazinium monochloride (0·0014 g; 2×10^{-5} mol) to this solution followed by boiling for 5 min gave a pale yellow solution which on cooling gave *cis*-$[Rh(phen)_2Cl_2]Cl,3H_2O$ [hereafter referred to as complex (A)] in 60—70% yield.

Exactly similar observations were made on carrying out the reaction of $[H_3O][Rh(phen)Cl_4]$ [9] (0·26 g) with phen (0·2 g) in aqueous solution. Thus no change in electronic spectrum resulted after boiling for 5 min, whereas addition of hydrazinium monochloride (0·001 g) followed by boiling for 5 min gave a yellow solution which gave a 65% yield of complex (A) on cooling. Similar observations were made when preparing *cis*-$[Rh(bipy)_2Cl_2]Cl,2H_2O$ [hereafter referred to as complex (B)].

The preparation described by Gillard *et al.*,[11] which involves the reaction of rhodium trichloride (1 mol) with aa (2·2 mol) in aqueous ethanol in the presence of hydrazinium monochloride (0·2 mol) using the same reaction times as described above, gave *cis*-$[Rh(aa)_2Cl_2]Cl$ in 60—70% yields.

2. *Catalysed Reaction with Phen* (2·0 *mol*). To a warm (*ca.* 40°) solution of rhodium trichloride (0·26 g) in water (5 ml) was added a warm solution of phen (0·4 g) in ethanol (5 ml). A flocculent brick-red precipitate was produced. Addition of hydrazinium monochloride (0·001 g) to this mixture followed by boiling for 10 min caused the precipitate to dissolve slowly. Cooling to *ca.* 80° gave a buff-coloured precipitate which was filtered off and on cooling the filtrate to room temperature a yellow crystalline solid was obtained. This latter solid was washed well with cold water giving a yellow filtrate and an insoluble buff precipitate. The physical and spectroscopic properties of the buff precipitates (0·14 g) were identical to those of authentic *cis*-$[Rh(phen)_2Cl_2][Rh(phen)Cl_4]$. The yellow filtrate, on concentration, gave complex (A) (0·14 g).

3. *Catalysed Reaction with Phen* (3·3 *mol*). Addition of phen (0·65 g) in warm (*ca.* 40°) ethanol (10 ml) to a warm solution of rhodium trichloride (0·26 g) in water (20 ml) gave a brick-red precipitate. Addition of hydrazinium monochloride (0·001 g) to this mixture, followed by boiling for 30 min, gave a pale brown solution. Addition of concentrated perchloric acid (0·1 ml) to this cooled solution gave a white crystalline precipitate (80% yield), the properties of which were identical to those of authentic $[Rh(phen)_3](ClO_4)_3,3H_2O$ prepared by the method [9] of McKenzie and Plowman. $[Rh(bipy)_3](ClO_4)_3,2H_2O$ was prepared in a similar way (77% yield). Boiling the above reaction mixture for 5 min instead of 30 min gave mainly *cis*-$[Rh(aa)_2Cl_2]^+$.

4. *In the Absence of Dioxygen.* Triply degassed acetone–water (1 : 1; 20 ml) was condensed onto a mixture of rhodium trichloride (0·263 g; 1×10^{-3} mol) and phen (0·66 g; $3{\cdot}3 \times 10^{-3}$ mol) in an evacuated (0·001 mmHg) flask containing a magnetic follower. The resulting suspension was stirred (*in vacuo*) at 25° for 10 days. Air was then admitted to the flask and addition of sodium perchlorate (0·2 g) to the pale yellow solution gave a pale yellow precipitate of complex (A) in 95% yield.

The similar reaction with bipy gave, on addition of sodium perchlorate, a pale yellow precipitate of complex (B) (17% yield) which was filtered off. Concentration of the filtrate to 5 ml followed by addition of ethanol gave a white precipitate of $[Rh(bipy)_3](ClO_4)_3$ (38% yield).

cis-*Di-iodobis*(1,10-*phenanthroline*)*rhodium*(III) *Iodide*, cis-$[Rh(phen)_2I_2]I$.—A solution of complex (A) (0·1 g) and sodium iodide (1·0 g) in aqueous ethanol (1 : 1; 40 ml) was

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* We have shown that the optical isomer of *cis*-$[Rh(phen)_2(OH)_2]^+$ is stable towards heat and base.[32] The loss of optical activity observed on base hydrolysis of *cis*-$[Rh(phen)_2Cl_2]^+$ must therefore occur during the hydrolysis rather than because of instability of the hydrolysis product.

[32] P. S. Sheridan, personal communication.

[33] J. I. Legg and B. E. Douglas, *Inorg. Chem.*, **1968**, **7**, **1452.**

boiled under reflux for 1 h. The resulting deep orange solution was concentrated to *ca.* 15 ml and allowed to cool whereupon light brown crystals (0·1 g) of *cis*-$[Rh(phen)_2I_2]I$ were obtained. The yield of product in the above reaction was not noticeably affected by addition of hydrazinium monochloride (*ca.* 0·001 g) or by use of t-butanol or acetone instead of ethanol. However, carrying out the above reaction in the absence of ethanol gave an insoluble yellow precipitate which had an electronic spectrum identical to that of complex (A): it would therefore appear to be *cis*-$[Rh(phen)_2Cl_2]I$.

Exactly similar results were obtained on carrying out the reaction of complex (B) with sodium iodide.

cis-*Chloroaquobis*(1,10-*phenanthroline*)*rhodium*(III) *Perchlorate Monohydrate*, cis-$[Rh(phen)_2Cl(OH_2)](ClO_4)_2,H_2O$.—An aqueous solution (10 ml) of complex (A) (0·1 g) and sodium hydroxide (0·1 g) was boiled vigorously for 2 min. To the cooled solution was added concentrated perchloric acid to give pH *ca.* 10 whereupon pale yellow crystals slowly formed: a further crop was obtained after standing at 5° for 2 days. Combination of these two crops followed by recrystallisation from water (*ca.* 10 ml) containing concentrated perchloric acid (*ca.* 0·1 ml) gave the product in 42% yield.

cis-$[Rh(bipy)_2Cl(OH_2)](ClO_4)_2,H_2O$ was prepared (40% yield) in exactly the same way starting with complex (B).

cis-*Diaquobis*(1,10-*phenanthroline*)*rhodium*(III) *Perchlorate Dihydrate*, cis-$[Rh(phen)_2(OH_2)_2](ClO_4)_3,2H_2O$.—A solution containing complex (A) (0·1 g), hydrazinium monochloride (0·001 g) and sodium hydroxide (0·1 g) in water (15 ml) was boiled for 10 min. Evaporation of this solution to *ca.* 5 ml, followed by neutralisation with concentrated perchloric acid gave a white precipitate which was redissolved by further careful addition of concentrated perchloric acid. This solution was concentrated to *ca.* 2·5 ml. After standing for a few days at 5° pale yellow crystals were obtained. Recrystallisation from water (*ca.* 5 ml) containing one drop of concentrated perchloric acid gave the product in 64% yield.

cis-$[Rh(bipy)_2(OH_2)_2](ClO_4)_3,H_2O$ was obtained in 60% yield using the same method as described above. The complex, *cis*-$[Rh(bipy)_2(OH)_2](OH),xH_2O$, used for n.m.r. studies, was obtained by passing a solution of *cis*-$[Rh(bipy)_2(OH_2)_2](ClO_4)_3$ down an anion exchange column in the hydroxide form. The eluent containing the rhodium complex was evaporated to dryness to give a pale yellow solid.

cis-*Dicyanobis*(1,10-*phenanthroline*)*rhodium*(III) *Chloride*, cis-$[Rh(phen)_2(CN)_2]Cl,2{\cdot}5H_2O$.*—A solution containing complex (A) (0·25 g) and sodium cyanide (0·06 g) in water (10 ml) was boiled vigorously until the solution became colourless (*ca.* 10 min). The solution was treated with concentrated hydrochloric acid (5 ml) and boiled for a further 2—3 min to remove hydrogen cyanide. On cooling, colourless crystals were obtained which were filtered off and recrystallised from water to give the product in 84% yield. *cis*-$[Rh(bipy)_2(CN)_2]Cl,4H_2O$ * was prepared in a similar way starting from complex (B). The sparingly soluble salts, *cis*-$[Rh(aa)_2(CN)_2]ClO_4,H_2O$, were prepared by addition of sodium perchlorate to an aqueous solution of the corresponding chloride salt. Heating an aqueous solution containing complex (A) (0·15 g) and sodium cyanide (0·1 g) at 90° for 1 h gave a pale yellow solution. Treatment with hydrochloric acid followed by concentration gave a precipitate. Recrystallisation from water gave pale yellow crystals which analysis indicated to be mainly *cis*-$[Rh(phen)_2Cl(CN)]Cl,H_2O$ (see Table 1).

cis-*Chloroamminebis*(1,10-*phenanthroline*)*rhodium*(III) *Perchlorate Monohydrate*, cis-$[Rh(phen)_2(NH_3)Cl](ClO_4)_2,H_2O$.—A solution containing complex (A) (0·12 g) and 8/80 ammonia (10 ml) in water (10 ml) was boiled vigorously for 5 min. Sodium perchlorate (0·2 g) was added to the resulting pale yellow solution which on concentration gave pale yellow crystals of the product (yield 78%). *cis*-$[Rh(bipy)_2(NH_3)Cl](ClO_4)_2,2H_2O$ was prepared using the same method as described above (yield 80%).

cis-*Diamminebis*(1,10-*phenanthroline*)*rhodium*(III) *Perchlorate Trihydrate*, cis-$[Rh(phen)_2(NH_3)_2](ClO_4)_3,3H_2O$.—An aqueous solution containing complex (A) (0·15 g), 8/80 ammonia (1 ml) and hydrazinium monochloride (0·001 g) was boiled vigorously for 5 min. To the cooled solution was added sodium perchlorate (0·2 g) and after standing at 5° for a few days light brown crystals were obtained. Recrystallisation from water (charcoal) gave colourless crystals of the product in 54% yield.

cis-$[Rh(phen)_2Cl(NO_2)]Cl,1{\cdot}5H_2O$.—Complex (A) (0·15 g) with sodium nitrite (0·05 g; 3 mol per mol Rh) in water (10 ml) was boiled vigorously for 5 min. Concentrated hydrochloric acid (3 ml) was added to the resulting pale yellow solution which was then boiled for a further 5 min to expel nitrogen dioxide. Very pale yellow crystals of the product were formed on cooling, yield 75%.

cis-$[Rh(bipy)_2Cl(NO_2)]Cl,2H_2O$ was prepared using the same method starting with complex (B). Aqueous solutions of *cis*-$[Rh(phen)_2Cl(NO_2)]Cl$ and the corresponding bipy complex became pink on standing for 1 h [*cf.* the development of a pink colour [14] in solid oxalate salts of phenanthrolinerhodium(III) complexes]. An increase in electrical conductivity also occurred. For this reason, the results reported in Table 2 refer to freshly prepared solutions.

cis-*Chloro*(*pyridine*)*bis*(1,10-*phenanthroline*)*rhodium*(III) *Perchlorate Monohydrate*, cis-$[Rh(phen)_2(py)Cl](ClO_4)_2,H_2O$.—Complex (A) (0·1 g) with pyridine (0·2 g) in water (15 ml) was boiled vigorously for 5 min. Addition of sodium perchlorate (0·2 g) to the cooled solution gave a dense precipitate which was recrystallised from water to give the product in 55% yield.

cis-$[Rh(bipy)_2(py)Cl](ClO_4)_2$ was prepared in exactly the same way starting from complex (B).

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* This preparation must be carried out in an efficient fume cupboard since HCN is evolved.