Synthesis and Characterisation of Rhodium(III) Complexes Containing Nitrogen Heterocyclic Ligands

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The synthesis and characterisation of complexes of the type *trans*-$[RhL_4X_2]Y$ (L = 3 or 4-substituted pyridine, 3,5-disubstituted pyridine, isoquinoline, pyrimidine, pyrazole, thiazole, X = Cl, Br and for L = py I; Y = univalent anion) are described. Using the same catalytic method, *N*-methylimidazole and ammonia give complexes of the type $[RhL_5X]^{2+}$ (X = Cl or Br), whereas 5-chloro- and 5-nitro-*N*-methylimidazole give complexes of the type *trans*-$[RhL_4X_2]^+$. All the complexes of the type *trans*-$[RhL_4X_2]^+$ and also $[RhL_5Cl]^{2+}$ (L = *N*-methylimidazole) undergo catalytic substitutions, and the nature of the products is discussed.

THE salts of *trans*-dihalogenotetrakispyridinerhodium-(III) have long been known [1] and the mechanism of their catalytic synthesis [2] and catalytic substitutions [3] still continues to arouse interest. It has recently been shown that such compounds exhibit a remarkable specific bacteriostatic activity [4] and we now describe the synthesis and characterisation of a series of compounds of the type *trans*-$[RhL_4X_2]Y$ (L = pyridine or substituted pyridine; X = Cl, Br, I; Y = univalent anion) which were required for investigations into their bacteriostatic activity. The related complexes *trans*-$[RhL_4X_2]^+$ (L = isoquinoline, pyrimidine, pyrazole, thiazole) are also described but attempts to prepare such compounds by similar catalytic methods with L = *N*-methylimidazole (miz) or ammonia always resulted in the formation of complexes of the type $[RhL_5X]^{2+}$. However, using 5-chloro- or 5-nitro-*N*-methylimidazoles, which are less basic than *N*-methylimidazole itself, complexes of the type *trans*-$[RhL_4X_2]^+$ have been obtained and are also described.

Synthesis and Characterisation of trans-$[RhL_4X_2]^+$.—The synthesis of complexes of the type *trans*-$[RhL_4X_2]^+$ (L = 3- or 4-substituted pyridine, 3,5-disubstituted pyridine, isoquinoline, pyrimidine, pyrazole, thiazole; X = Cl, Br) is achieved by the general catalytic methods developed earlier [5,6] involving the use of a two-electron

[1] S. M. Jørgensen, *J. prakt. Chem.*, 1883, **27**, 478.
[2] J. V. Rund, *Inorg. Chem.*, 1968, **7**, 24.
[3] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1971, 1840.
[4] R. J. Bromfield, R. H. Dainty, R. D. Gillard, and B. T. Heaton, *Nature*, 1969, **223**, 735.
[5] R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1965, 1951.
[6] R. D. Gillard, J. A. Osborn, P. B. Stockwell, and G. Wilkinson, *Proc. Chem. Soc.*, 1964, 284.

reducing agent on an aqueous mixture of the ligand and rhodium trihalide.

We have, however, been unable to obtain the tetrakis-complexes with certain ligands which fall into several types. The first contained the substituent in the 2-position (*e.g.* α-picoline, 2,4-lutidine, 2-aminopyridine), and we attribute our failure to produce these complexes to steric hindrance. It is known that the cation *trans*-$[Rh(py)_4Cl_2]^+$ adopts the configuration of a four-bladed propeller in its hydrogen dinitrate salt [7] and substitution in the 2-position of the pyridine ring will decrease the strength of the Rh–N bonds not only by increasing the non-bonding interaction of the 2-substituents but also by increasing the dihedral angle and thus decreasing any π-component of the Rh–N bonds. Attempted preparations of octahedral nickel(II) complexes containing 2-substituted-pyridine ligands were also unsuccessful.[8] The same effects are found in the quinoline series. Thus, although tetrakis-complexes with isoquinoline could be prepared, we have been unable to obtain tetrakis-complexes with quinoline. Similar reasoning has been advanced to explain the instability of *trans*-$[Rh(py)_4I_2]^+$ which has previously only been prepared ' with difficulty '.[9] This complex, although less stable than *trans*-$[Rh(py)_4X_2]^+$ (X = Cl or Br) can readily be prepared by using very mild reaction conditions.

In some cases reactions of the organic ligand occurred preferentially. Thus tetrakis-complexes with 3-formylpyridine could be isolated whereas the following reaction occurred with 4-formylpyridine: [10]

trans-$[Rh(4\text{-}CHO\cdot py)_4Cl_2]Cl + 4H_2O \longrightarrow$ *trans*-$[Rh(4\text{-}CH(OH)_2py)_4Cl_2]Cl$

In the case of 3- or 4-cyanopyridine, the bifunctional nature of the ligand produced insoluble polymeric products. A similar polymeric product was obtained using pyrazine whereas tetrakis-complexes have been obtained with the potentially bifunctional ligands pyrimidine, thiazole, and pyrazole.

Nevertheless despite these above restrictions we have been able to prepare the salts listed in Table 1. They have been characterised through analysis, conductivity measurements (typical of 1 : 1 electrolytes), and electronic spectroscopy; the last named is particularly useful since the $^1E_g \leftarrow {}^1A_{1g}$ component for *trans*-$[RhL_4X_2]^+$ (L = *N*-bonded ligand; X = Cl or Br) occurs at 409 ± 2 and 439 ± 2 nm respectively.

For complexes containing symmetrically substituted pyridines, the ^1H n.m.r. spectra are readily assigned. Thus for *trans*-$[Rh(4\text{-methylpyridine})_4Cl_2]^+$, at 60 MHz, the methyl resonance is a sharp singlet at τ 7·42 and the resonance due to the α- and β-hydrogens are relatively sharp doublets at τ 1·60 and 2·58 respectively. However, it is possible for complexes containing unsymmetrically substituted pyridines, *e.g.* *trans*-$[Rh(3\text{-methylpyridine})_4Cl_2]^+$ to adopt different geometrical configurations depending on the orientation of the substituted pyridine in the four-bladed propeller-shaped molecule. Molecular models suggest a high barrier to rotation of the pyridine ligand about the Rh–N axis and any rotation would appear to involve a concerted flip of all four pyridine ligands. It is thus to be expected that the equilibrium mixture, which presumably results from the preparative route, should contain a statistical distribution of such conformers, which is supported by *X*-ray structural determination of *trans*-$[Ni(3,4\text{-dimethylpyridine})_4](ClO_4)_2$ [11] and $[M(py)_4Cl_2]$ (M = Co or Ni).[12] It has, however, proved impossible to distinguish these conformers by n.m.r. techniques. Thus, the methyl resonance of *trans*-$[Rh(3\text{-methylpyridine})_4Cl_2]^+$, at 220 MHz, is a single sharp line (τ 7·65) and only two types of α-hydrogens could be observed (a singlet at τ 1·80 and a doublet at τ 1·76). We attribute this to the difference

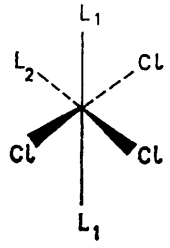


FIGURE 1

in chemical shift between similar hydrogen atoms in different conformations being too small to be detected rather than to free rotation of the pyridine ligands. This receives further support by examination of the spectra of complexes of the type 1,2,6-$[RhL_3Cl_3]$ which, molecular models suggest, should also exhibit restricted rotation of the pyridine ligands. However, they never show more than two groups of resonances (see Table 2) in the ratio 2 : 1 due to L_1 and L_2 respectively (see Figure 1) even at 220 MHz. Furthermore, at 60 MHz, the aromatic region of the spectrum of 1,2,6-$[Rh(4\text{-n-propylpyridine})_4Cl_2]^+$ in deuteriochloroform solutions remains unchanged from +40 to −75° except for slight loss of resolution due to increased viscosity at low temperatures. Similarly, the n.m.r. spectrum of 1,2,3-$[Rh(py)_3Cl_3]$ in $[^2H_6]$dimethyl sulphoxide at 60 MHz shows all the ligands to be equivalent and resonances due to α-, β-, and γ-protons occur at τ 1·53(2), 2·28(2), and 1·73(1) respectively.

Synthesis and Characterisation of N-*Methylimidazole and Substituted* N-*Methylimidazole Rhodium*(III) *Complexes.*—Because of steric constraints imposed by placing five or six pyridine ligands around a metal ion there are few reported examples of complexes of the type $[M(py)_5X]^{n+}$ or $[M(py)_6]^{m+}$. The only well authenticated examples are $[Fe(py)_6]^{2+}$ which is shown to have T_h

[7] G. C. Dobinson, R. Mason, and D. R. Russell, *Chem. Comm.*, 1967, 62.
[8] L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 265.
[9] B. N. Figgis, R. D. Gillard, R. S. Nyholm, and G. Wilkinson, *J. Chem. Soc.*, 1964, 5189.
[10] R. D. Gillard and B. T. Heaton, *J. Chem. Soc.* (*A*), 1968, 1405.
[11] F. Madaule-Aubry, W. R. Busing, and G. M. Brown, *Acta Cryst.*, 1968, **B24**, 754.
[12] M. A. Poraj-Koschits, *Trav. Inst. Crist.*, 1954, **10**, 302; *idem*, *Acta Cryst.*, 1957, **10**, 784.

symmetry by *X*-ray crystallography,[13] $[Ni(py)_6]^{2+}$, which electronic spectra suggest is present in solution,[14] and the briefly reported $[Ru(py)_6]^{2+}$.[15]

Since the steric requirements of *N*-methylimidazole are similar to those of pyridine, it was somewhat surprising to find that addition of *N*-methylimidazole to a warm aqueous ethanol solution of rhodium trichloride resulted in the formation of $[Rh(miz)_5Cl]^{2+}$. Starting from rhodium tribromide instead of rhodium trichloride, $[Rh(miz)_5Br](ClO_4)_2$ has been isolated, although not in good yield.

For complexes of the type 1,2,6-$[RhL_3Cl_3]$ (L = substituted pyridine), the α-protons of L_1 and L_2 (see Figure 1) always show the largest difference in chemical shift and this is always accompanied by the resonances occurring at lower field than in the free ligand. Similar trends were therefore expected for the complex $[Rh(miz)_5Cl]^{2+}$. The proton chemical shifts of miz are dependent on both concentration and solvent. Similar shifts have also been found with their rhodium(III) complexes and in order to minimise such effects and to optimise solubility and resolution the n.m.r. spectra of the complexes and the free ligands [16] have been measured in [$^2H_6$]dimethyl sulphoxide–[^2H]chloroform (1 : 1). The

TABLE 1

Some properties of complexes of the type *trans*-$[RhL_4X_2]Y,xH_2O$

L	X	Y	*x*	$\lambda_{max.}$	ε	Λ †		Formula	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N	Recrystallised from
Pyridine	Cl	Cl	5	409	100	95·5 *	77·5	$C_{20}H_{30}Cl_3N_4O_5Rh$	38·7	5·2	8·9	39·0	4·9	9·1	*a*
Pyridine	Br	Br	5	439	118	106 *	69·0	$C_{20}H_{30}Br_3N_4O_5Rh$	32·0	4·0	7·5	31·7	3·8	7·7	*a*
Pyridine	I	I	5	485sh	*ca.* 600	107 *		$C_{20}H_{30}I_3N_4O_5Rh$	26·9	3·2	6·1	27·0	3·4	6·3	*b*
				401	9100										
Pyridine	I	ClO_4	0	490sh	*ca.* 440		88	$C_{20}H_{20}ClI_2N_4O_4Rh$	32·2	3·2	8·0	31·1	2·6	7·2	*e*
3-Methylpyridine	Cl	Cl	1	409	100		73·0	$C_{24}H_{30}Cl_3N_4ORh$	48·0	5·0		47·5	5·0		*b*
3-Methylpyridine	Br	Br	1	441	120		77·5	$C_{24}H_{30}Br_3N_4ORh$	39·3	4·4		39·9	4·1		*b*
4-Methylpyridine	Cl	Cl	3	409	98		77·5	$C_{24}H_{34}Cl_3N_4O_3Rh$	45·35	5·4		45·4	5·5		*b*
4-Methylpyridine	Cl	ClO_4	0	411	87		75	$C_{24}H_{28}Cl_3N_4O_4Rh$	44·5	4·3	8·7	44·6	4·4	8·7	*b*
4-Methylpyridine	Cl	BF_4	0	411	90		90	$C_{24}H_{28}BCl_2F_4N_4Rh$	45·4	4·6	9·1	45·5	4·5	8·9	*b*
4-Methylpyridine	Br	Br	2	439	115		77·5	$C_{24}H_{32}Br_3N_4O_2Rh$	38·35	4·3		38·4	4·4		*b*
3-Ethylpyridine	Cl	Cl	2	410	95		73·0	$C_{28}H_{40}Cl_3N_4O_2Rh$	49·9	6·0		49·8	5·9		*b*
3-Ethylpyridine	Br	Br	1	440	115		71·0	$C_{28}H_{38}Br_3N_4ORh$	42·6	4·85		42·75	4·95		*b*
4-Ethylpyridine	Cl	ClO_4	0	409	100		75·0	$C_{28}H_{36}Cl_3N_4O_4Rh$	48·1	4·9	7·9	47·9	5·2	8·0	*b*
4-Ethylpyridine	Br	Br	1	438	180		77·5	$C_{28}H_{38}Br_3N_4ORh$	42·6	4·85		42·4	5·0		*b*
4-n-Propylpyridine	Cl	NO_3	0	409	100		82·5	$C_{32}H_{44}Cl_2N_5O_3Rh$	53·3	6·3		53·2	6·1		*b*
4-n-Propylpyridine	Br	NO_3	0	441	155		69·0	$C_{32}H_{44}Br_2N_5O_3Rh$	47·5	5·5		47·5	5·5		*b*
4-Isopropylpyridine	Br	Br	4	441	130		77·5	$C_{32}H_{52}Br_3N_4O_4Rh$	43·6	5·95		43·2	5·7		*b*
4-n-Butylpyridine	Cl	ClO_4	0	410	95		69·0	$C_{36}H_{52}Cl_3N_4O_3Rh$	53·5	6·45	6·9	53·1	6·8	7·1	*c*
3,5-Dimethylpyridine	Cl	Cl	0	410	90		73·0	$C_{28}H_{36}Cl_3N_4Rh$	52·7	5·7		52·9	5·8		*b*
3-Aminopyridine	Cl	Cl	0	410	*ca.* 140	83 *		$C_{20}H_{24}Cl_3N_8Rh$	41·0	4·1	19·1	40·4	4·4	19·0	*a*
3-Aminopyridine	Br	Br	0	440	*ca.* 120	85 *		$C_{20}H_{24}Br_3N_8Rh$	32·9	3·6		33·4	3·4		*a*
4-Aminopyridine	Cl	Cl	2	410	*ca.* 100	95·5 *		$C_{20}H_{28}Cl_3N_8O_2Rh$	38·4	4·55		38·6	5·0		*a*
4-Aminopyridine	Br	Br	2	440	*ca.* 120	98 *		$C_{20}H_{28}Br_3N_8O_2Rh$	34·4	4·0		34·25	4·4		*a*
3-Chloropyridine	Cl	Cl	5	410	106		52	$C_{20}H_{26}Cl_7N_4O_5Rh$	32·1	3·4	7·3	31·9	3·5	7·4 ‡	*d*
4-(1-hydroxypropyl)-pyridine	Cl	ClO_4	0	409	103	103 *		$C_{32}H_{44}Cl_3N_4O_8Rh$	46·7	5·4	6·8	46·2	5·4	6·8	*b*
Pyridine-4-carboxylic acid	Cl	Cl	3	410	*ca.* 110			$C_{24}H_{26}Cl_3N_4O_{11}Rh$	38·15	3·5	7·4	38·4	4·0	7·5	*a*
3-Acetylpyridine	Cl	ClO_4	0	408	87		68	$C_{28}H_{28}Cl_3N_4O_8Rh$	43·8	3·7	7·2	44·4	3·7	7·4	*b*
Isoquinoline	Cl	Cl	3	410	102		61	$C_{36}H_{28}Cl_3N_4O_3Rh$	55·1	3·8	7·3	55·4	4·4	7·2	*e*
Thiazole	Cl	Cl	5	409	89		77	$C_{12}H_{22}Cl_3N_4O_5RhS_4$	22·5	3·6	9·0	22·5	3·5	8·8	*e*
Thiazole	Br	Br	2	440	144		73	$C_{12}H_{16}Br_3N_4O_2RhS_4$	20·2	3·0	7·9	20·0	2·2	7·8	*e*
Pyrazole	Cl	Cl	5	407	88	77 *		$C_{12}H_{22}Cl_3N_8O_5Rh$	25·2	4·6	19·6	25·2	4·6	19·6	*e*
Pyrimidine	Cl	ClO_4	0	409	105		47	$C_{16}H_{16}Cl_3N_8O_4Rh$	32·4	2·7	18·9	32·4	2·7	18·9	*e*

[a] Water. [b] Water–ethanol. [c] Water–ethanol–acetone. [d] Ethanol. [e] Water–methanol.

† Conductivity (Ω^{-1} cm^2 mol^{-1}) of *ca.* 10^{-3}M-nitromethane solutions or * aqueous solutions.
‡ Found: Cl, 32·9. Required Cl, 32·9%.

TABLE 2

Proton chemical shifts (τ) at 220 MHz for complexes of the type 1,2,6-$[RhL_3Cl_3]$ (see Figure 1)

L	Solvent	L_1 α	L_1 β	L_1 γ	L_2 α	L_2 β	L_2 γ
Pyridine	$CDCl_3$	1·30(d)	2·48(c)	1·97(c)	1·60(d)	2·48(c)	1·97(c)
3,5-Dimethylpyridine	$(CD_3)_2SO$	1·68(s)	7·74(s)	2·32(s)	2·02(s)	7·78(s)	2·27(s)
4-Methylpyridine	$CDCl_3$	1·28(d)	2·90(d)	7·58(s)	1·59(d)	2·90(d)	7·58(s)
3-Methylpyridine	$CDCl_3$	1·19(s), 1·43(d)	2·87(c), 7·70(s)	2·38(d)	1·59(d), 1·59(s)	2·87(s), 7·74(s)	2·31(d)

(s) = Singlet. (d) = Doublet. (c) = Complex pattern.

[13] L. F. Dahl and R. J. Doedens, *J. Amer. Chem. Soc.*, 1966, **88**, 4847.
[14] M. R. Roserthal and R. S. Drago, *Inorg. Chem.*, 1965, **4**, 840.
[15] P. T. Cheng, B. R. Loescher, and S. C. Nyburg, *Inorg. Chem.*, 1971, **10**, 1275.
[16] G. B. Barlin and T. J. Batterham, *J. Chem. Soc.* (*B*), 1967, 516.

60 MHz n.m.r. spectrum of $[Rh(miz)_5Cl](ClO_4)_2$ is consistent with the structure shown in Figure 2, although

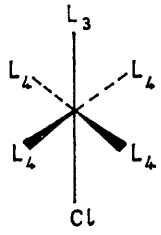


FIGURE 2

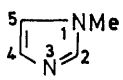


FIGURE 3

since H^4 (see Figure 3) on L_3 and L_4 occur at different chemical shifts, it might have been expected that H^2 on L_3 and L_4 would have also occurred at different chemical shifts.

Assuming that the mechanism of formation of *trans*-$[RhL_4X_2]^+$ and $[RhL_5X]^{2+}$ is the same, then the reason for the formation of $[RhL_5X]^{2+}$ instead of *trans*-$[RhL_4X_2]^+$ when L = ammonia or miz must be a reflection of the strengths of the Rh–N bonds so formed.

ethanol solution (pH 3) of $[Rh(miz)_5Cl]^{2+}$ with excess sodium chloride.

The reactions (1)—(3) are rapid in the presence of

$$[Rh(miz)_5Cl]^{2+} \xrightarrow{Cl^-/pH\ 3} [Rh(miz)_4Cl_2]^+ \quad (1)$$

$$[Rh(miz)_4Cl_2]^+ \xrightarrow{L} [Rh(miz)_5Cl]^{2+} \quad (2)$$

$$[Rh(miz)_4Cl_2]^+ \xrightarrow{Br^-} [Rh(miz)_4Br_2]^+ \quad (3)$$

ethanol or absence of oxygen at 80°, and are thus analogous to the substitutions of *trans*-$[Rh(py)_4Cl_2]^+$, which have been shown to involve rhodium(I) and rhodium(III) hydrido-species,[3] and to the catalysed substitutions of $[Pt(NH_3)_5X]^{3+}$ (X = Cl, Br, I).[23,24]

Utilising these conditions, all the complexes in Table 1 have been found to undergo catalytic substitution, but only the catalytic reactions of *trans*-$[Rh(py)_4X_2]^+$ with other univalent anions (F^-, I^-, N_3^-, CNO^-, NO_2^-, SCN^-) have been investigated in detail and the nature of these products is now described.

Substitution Products of trans-$[Rh(py)_4X_2]^+$ *with Other Anions.*—(a) *Reaction with halides.* It has previously been shown that rapid and complete halogen interchange is accomplished by boiling an aqueous ethanol solution of *trans*-$[Rh(py)_4X_2]^+$ (X = Cl or Br) with bromide and chloride respectively.[3] The mechanism of this reaction has been shown to involve a reduced co-ordinatively unsaturated Rh^I species which is kinetically inactive in acidic solutions due to the complete conversion to Rh^{III}–H species.[25] These ideas receive further support since on boiling an aqueous ethanol solution of *trans*-$[Rh(py)_4Cl_2]Cl$ with a large excess of bromide in hydrobromic acid (6M) for 1 h, there was no evidence for the formation of *trans*-$[Rh(py)_4Br_2]^+$. Indeed it was possible to isolate in high yield *trans*-$[Rh(py)_4Cl_2][H_5O_2]Br_2$.

The reaction of *trans*-$[Rh(py)_4X_2]^+$ (X = Cl or Br) with

TABLE 3

Proton chemical shifts (τ) at 60 MHz for *N*-methylimidazole, (miz), 5-substituted *N*-methylimidazole and their rhodium(III) complexes in 50 : 50 $CDCl_3$–$(CD_3)_2SO$ (unless stated otherwise); solutions of the complexes are *ca.* 0·1M and ligand solutions are 0·4M

Compound	H^2	H^4	H^5	H^{Me}
N-Methylimidazole (miz)	2·53(1) 2·43(1) 2·38(1) 2·50(1)	2·92(1) 2·92(2) [b] 2·93(2) [c] 2·98(1)	3·12(1) 3·07(1)	6·30(3) [a] 6·31(3)
$[Rh(miz)_5Cl](ClO_4)_2$	2·12(5)	2·53(1), 2·69(4)	3·35(5)	6·18(15)
$[Rh(miz)_4Cl_2]ClO_4$	2·00(1)	2·80(1)	2·87(1)	6·21(3)
5-Chloro-*N*-methylimidazole (A)	2·34(1)	3·08(1)		6·37(3)
trans-$[RhA_4Cl_2]Cl$	1·66(1)	2·77(1)		6·26(3)
5-Nitro-*N*-methylimidazole (B)	2·04(2)			6·00(3)
trans-$[RhB_4Cl_2]ClO_4$	1·39(1)	1·76(1)		5·93(3)

[a] In $CDCl_3$.[16] [b] In nitromethane.[16] [c] In dioxan.[16]

Thus, whereas ammonia and miz (pK_a 9·5 [17] and 7·20 [18] respectively) form $[RhL_5X]^{2+}$ on reaction with aqueous ethanolic rhodium trihalide, the less basic ligands, pyridine, 5-nitro-*N*-methylimidazole, and 5-chloro-*N*-methylimidazole (pK_a 5·3,[17] and 2·13 [19] and 4·75 [20] respectively) give *trans*-$[RhL_4X_2]^+$.

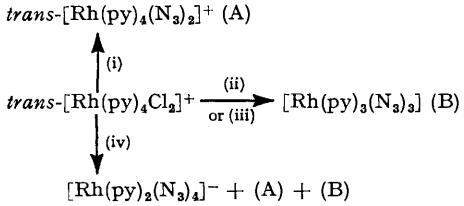
Similar behaviour has been found for nickel(II).[21,22] Thus, whereas ammonia and imidazole form complexes of the type $[NiL_6]^{2+}$ (L = ammonia, imidazole), when L = py or 4(5)-bromoimidazole (pK_a 3·6) complexes of the type $[NiL_4Cl_2]$ are formed.

Attempts to prepare $[Rh(miz)_4Cl_2]^+$ by the reaction of miz (4 mol. equiv.) with an aqueous ethanol solution of rhodium trichloride (1 mol. equiv.) always resulted in the formation of $[Rh(miz)_5Cl]^{2+}$. However, *trans*-$[Rh(miz)_4Cl_2]^+$ can be prepared by boiling an aqueous

[17] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, 1968, p. 140.
[18] N. C. Li, J. M. White, and E. Doody, *J. Amer. Chem. Soc.*, 1954, **76**, 6219.
[19] A. Grimison, J. H. Ridd, and B. V. Smith, *J. Chem. Soc.*, 1960, 1352.
[20] G. G. Gallo, C. R. Pasqualucci, P. Radaelli, and G. C. Lancini, *J. Org. Chem.*, 1964, **29**, 862.
[21] W. J. Eilbeck, F. Holmes, and A. E. Underhill, *J. Chem. Soc.* (*A*), 1967, 757.
[22] W. J. Eilbeck, F. Holmes, C. E. Taylor, and A. E. Underhill, *J. Chem. Soc.* (*A*), 1968, 1189.
[23] F. Basolo, M. L. Morris, and R. G. Pearson, *Discuss. Faraday Soc.*, 1960, **29**, 80.
[24] W. R. Mason and R. C. Johnson, *Inorg. Chem.*, 1965, **4**, 1258.
[25] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1970, 3126.

fluoride is found to be rapid, even in the absence of catalysts. On heating an aqueous solution of *trans*-$[Rh(py)_4Br_2]^+$ (pH 6·5) with an excess of potassium fluoride, the electronic spectrum showed the disappearance of the 441 nm band ($t_{\frac{1}{2}}$ *ca.* 5 min) and the appearance of a band at 365 nm (isosbestic points were observed at 365 and 413 nm). The product, after separation from potassium fluoride by dialysis, was obtained as yellow crystals as the perchlorate salt and has been shown to be *trans*-$[Rh(py)_4Br(OH)]ClO_4$. This ready fluoride-assisted hydrolysis probably involves ion-pair formation as recently discussed by Pöe *et al.*[26] since the rate of hydrolysis of *trans*-$[Rh(py)_4Br_2]^+$ at 100° and pH 12—13 is very slow, although addition of ethanol to this solution does result in the rapid formation of *trans*-$[Rh(py)_4Br(OH)]^+$. Similar reactions occur with *trans*-$[Rh(py)_4Cl_2]^+$, although at a slower rate under comparable conditions. However, the best way of preparing complexes of the type *trans*-$[Rh(py)_4X(OH)]^+$ involves boiling a solution of *trans*-$[Rh(py)_4X_2]^+$ with excess acetate (see Experimental section). The position of $\lambda_{max.}$ for *trans*-$[Rh(py)_4X(OH)]^+$ (X = Cl, $\lambda_{max.}$ 359, ε 130; X = Br, $\lambda_{max.}$ 371, ε 180) compare favourably with those of the analogous ethylenediamine complexes,[27] and the corresponding aquo-complexes, *trans*-$[Rh(py)_4X(OH_2)]^{2+}$ could be obtained by recrystallising *trans*-$[Rh(py)_4X(OH)]^+$ from perchloric acid. The pK_a values (X = Cl or Br) of 4·00 ± 0·05 and 4·21 ± 0·05 respectively are much lower than those for the corresponding *trans*-$[Rh(en)_2X(OH_2)]^{2+}$ complexes [27] and may be a reflection of pyridine being a weaker base than ethylenediamine. Heating a solution of *trans*-$[Rh(py)_4Br(OH)]^+$ with hydrochloric acid gave *trans*-$[Rh(py)_4BrCl]^+$ which was isolated as the tetrafluoroborate salt.

(b) *Reaction with azide.* The di-, tri- and tetra-azido-rhodium–pyridine complexes have been isolated and their preparations are summarised in the Scheme.



SCHEME

(i) Aqueous solution boiled with N_3^- (2·3 mol).
(ii) Bubble nitrogen through a cold aqueous ethanol solution containing excess N_3^-.
(iii) To a cold aqueous solution containing excess N_3^- add a trace of BH_4^-.
(iv) To a hot aqueous solution containing excess N_3^- add a trace of BH_4^-.

Stereochemical requirements suggest that $[Rh(py)_4(N_3)_2]^+$ has a *trans*-configuration. This is supported by both the i.r. spectrum, which shows only one ν(N≡N) 2010 cm^{-1}, and the electronic spectrum ($\lambda_{max.}$ 386 nm, ε 1340), which is similar to *trans*-$[Rh(en)_2(N_3)_2]^+$ ($\lambda_{max.}$ 375 nm, ε 780).[28] The electronic spectra are of no assistance in assigning the stereochemistry of the other azido-complexes since they consist of rather broad unresolved bands. However, $[Rh(py)_3(N_3)_3]$, which was too insoluble to obtain a ^1H n.m.r. spectrum, probably has the 1,2,6-configuration since the ^1H n.m.r. of the related complex, [Rh(4-methylpyridine)$_3$$(N_3)_3$] showed two sets of resonances for the α- and β-protons [τ 1·6(2), 1·74(1); 2·76(2), 2·85(1) respectively] in the ratio 2 : 1. Whereas Basolo and his co-workers [29] found that Ru^{III} and Ir^{III} azido-ammines gave nitrogen and co-ordinated nitrene on treatment with dilute sulphuric acid, we have found no evidence for nitrogen evolution on addition of either H_2SO_4 or HCl to any of these azido-complexes.

(c) *Thiocyanate.* By warming an aqueous solution of *trans*-$[Rh(py)_4Cl_2]^+$ with an excess of thiocyanate either in the absence of oxygen or in the presence of ethanol a very insoluble yellow crystalline compound has been obtained. It has been shown by analysis, electronic spectroscopy in dimethyl sulphoxide ($\lambda_{max.}$ 409 nm, ε 98) and i.r. spectroscopy ν(Rh–Cl) 365 cm^{-1} to be *trans*-$[Rh(py)_4Cl_2]SCN$.

Using more forcing conditions (addition of a trace of BH_4^- to an aqueous solution containing an excess of thiocyanate), sulphurous odours and a yellow colloidal suspension was obtained. It is thus very surprising that we have been unable to induce catalytically either thiocyanate or iso-thiocyanate substitution since [Rh(py)$_3$$(SCN)_3$] is known but has previously been prepared from $[Rh(SCN)_6]^{3-}$ and pyridine.[30]

(d) *Cyanate.*—Whether by merely heating an aqueous solution of *trans*-$[Rh(py)_4Cl_2]^+$ with an excess of sodium cyanate or by reactions catalysed by ethanol or borohydride identical products were obtained as yellow plates. The possibility of hydrolysis of cyanate, suggested the possibility of the product being an ammine complex. However, the i.r. spectrum of the product showed ammonia to be absent and there were strong bands at 2235, 2190 cm^{-1} due to ν(C≡N) and a weaker band at 590 cm^{-1} due to δ(NCO). It was a non-electrolyte and analytical data showed it to have the composition $Rh(py)_3Cl(NCO)_2$. That it is a pure compound rather than a mixture of $[Rh(py)_3Cl_2(NCO)]$ and [Rh(py)$_3$$(NCO)_3$] is implied since it has not been possible to prepare either of these compounds. The i.r. spectrum is consistent with a *cis*-configuration and with a *N*-bonded NCO group.[31]

(e) *Nitrite.*—The addition of a trace of borohydride to a warm aqueous ethanol solution of *trans*-$[Rh(py)_4Cl_2]^+$ containing an excess of nitrite gives pale cream crystals of a non-electrolyte which analyses for $[Rh(py)_3(NO_2)_3]$. The i.r. spectrum shows the absence of the 1075 cm^{-1}

[26] H. L. Bott, A. J. Pöe, and K. Shaw, *J. Chem. Soc.* (*A*), 1970, 1745.
[27] H. L. Bott and A. J. Pöe, *J. Chem. Soc.* (*A*), 1967, 205.
[28] S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1962, **1**, 925.
[29] L. A. P. Kane-Maguire, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1969, **91**, 4609.
[30] J. Meyer and H. Kienitz, *Z. anorg. Chem.*, 1939, **242**, 281.
[31] J. L. Burmeister, *Co-ordination Chem. Rev.*, 1968, **3**, 225.

found in nitrito-complexes [32] and thus the NO_2-group may be assumed to be *N*-bonded.

EXPERIMENTAL

I.r. spectra (4000—400 cm^{-1}) were recorded as Nujol mulls on a Perkin-Elmer 457 spectrometer and (400—100 cm^{-1}) on a R.I.I.C. FS 720 spectrometer fitted with a transform FTS 100–7 computer. N.m.r. spectra at 60 MHz were recorded on a Perkin-Elmer R10 spectrometer at 33·5° and at 220 MHz on a Varian 220 spectrometer at 13°. U.v. and visible spectra were measured on a Unicam SP 800 spectrometer using matched 1 cm silica cells. Conductivity measurements were carried out at 25° using a Phillips PR 9500 bridge. Microanalytical determinations were carried out by the Microanalytical Laboratory of this department and by Dr. A. Bernhardt, Germany. Rhodium trichloride was obtained from Johnson Matthey and Co. Ltd. All the substituted pyridines were obtained from Reilly Chemicals and were used without further purification. *N*-Methylimidazole was obtained from Emmanuel and 5-chloro-*N*-methylimidazole was prepared by Wallach's reaction,[33] b.p., 204—205°. 5-Nitro-*N*-methylimidazole picrate was prepared using the methods described.[34,35] It converted into 5-nitro-*N*-methylimidazole by boiling it with hydrochloric acid (4M), followed by ether extraction of the aqueous layer until colourless (to remove picric acid), addition of base to the aqueous layer followed by ether extraction. This ether extract was concentrated to give colourless prisms of the product which were recrystallised from ether (charcoal), m.p. 59—60° (Found: C, 38·0; H, 4·2; N, 33·3. $C_4H_5O_2N_3$ requires C, 37·8; H, 4·0; N, 33·1%).

Preparation of Complexes of the Type trans-$[RhL_4X_2]Y$.—The following method has been used for all the complexes listed in Table 1. A solution of rhodium trihalide (1 mol) in aqueous ethanol (30%) was heated to boiling with the substituted pyridine or heterocyclic ligand (4·1 mol). After dissolution of the red-brown precipitate, a yellow-orange solution was formed which on cooling and concentration yielded a yellow-orange solid which was recrystallised from the solvents indicated in Table 1 to give the product usually in 70—90% yield. Salts containing other anions were obtained by addition of the appropriate acid to a solution of the complex in water.

trans-*Di-iodotetra(pyridine)rhodium*(III) *Iodide*, trans-$[Rh(py)_4I_2]I,5H_2O$.—Hydrogen was bubbled through a suspension of rhodium tri-iodide (0·1 g) in water (20 ml)–pyridine (40 ml)–ethanol (20 ml) whereupon the solution became brown. The unchanged material was filtered off and the filtrate was concentrated, *in vacuo*, at 25° to a final volume of *ca.* 20 ml when golden brown crystals of the product as the pentahydrate were obtained (0·07 g).

trans-*Dichlorotetra(pyridine)rhodium*(III) *Bromide Hydrogen Bromide Trihydrate*, trans-$[Rh(py)_4Cl_2]Br,HBr,3H_2O$.—A solution of *trans*-$[Rh(py)_4Cl_2]Cl,5H_2O$ (0·2 g), (I), in 30% aqueous ethanol (20 ml) containing sodium bromide (2 g) and 10M-HBr (30 ml) was heated at 70° for 1 h. Concentration of this solution after filtration resulted in the formation of large yellow crystals of the product which were filtered off, washed with a little water, ethanol, and ether and then air-dried; yield 0·11 g. A 10^{-2}M-solution of this complex in water had pH 2. The far-i.r. spectrum showed a strong band at 365 cm^{-1} due to ν(Rh–Cl) (Found: C, 33·6; H, 3·2; N, 8·2. $C_{20}H_{27}Br_2Cl_2N_4O_3Rh$ requires C, 34·1; H, 3·8; N, 8·0%).

trans-*Bromoaquotetra(pyridine)rhodium*(III) *Perchlorate Dihydrate*, trans-$[Rh(py)_4Br(OH_2)](ClO_4)_2,2H_2O$.—A 4M-sodium acetate solution (60 ml) containing *trans*-$[Rh(py)_4Br_2]Br,5H_2O$ (1·0 g), (II), was heated at 90° until the band at 439 nm in the electronic spectrum had moved to 370 nm (usually *ca.* 15 min). To the resulting solution was added sodium perchlorate (5 g) and the voluminous yellow precipitate was filtered off and recrystallised from 10M-perchloric acid to give orange-red prisms. These were filtered off and recrystallised from 1M-perchloric acid to give the desired product (0·4 g) (Found: C, 31·6; H, 3·4; N, 7·5; Br, 11·4. $C_{20}H_{26}BrCl_2N_4O_{11}Rh$ requires C, 31·9; H, 3·5; N, 7·5; Br, 11·2%). Desiccation of this complex for 1 week over H_2SO_4 resulted in the loss of water of crystallisation (Found: C, 33·3; H, 3·5; N, 7·7; Br, 10·3; Cl, 9·3. $C_{20}H_{22}BrCl_2N_4O_9Rh$ requires C, 33·5; H, 3·1; N, 7·8; Br, 11·1; Cl, 9·3%).

trans-*Bromohydroxotetra(pyridine)rhodium*(III) *Perchlorate*, trans-$[Rh(py)_4Br(OH)]ClO_4$.—Neutralisation of an aqueous solution (25 ml) of *trans*-$[Rh(py)_4Br(OH_2)](ClO_4)_2,2H_2O$ (0·2 g) with 0·1M-sodium hydroxide, followed by concentration yielded the desired product as orange-yellow prisms; yield 0·15 g (Found: C, 38·7; H, 3·6; N, 9·6; Br, 12·7; Cl, 5·5. $C_{20}H_{21}BrClN_4O_5Rh$ requires C, 39·0; H, 3·4; N, 9·1; Br, 13·0; Cl, 5·8%).

trans-*Chloroaquotetra(pyridine)rhodium*(III) *Perchlorate Hydrate*, trans-$[Rh(py)_4Cl(OH_2)](ClO_4)_2H_2O$.—This compound was prepared as for the bromo-analogue described above starting from (I) and stopping the reaction on minimisation of absorbance at 390 nm when the peak at 409 nm had disappeared and a peak at *ca.* 360 nm had appeared (Found: C, 32·8; H, 3·8; N, 7·7; Cl, 15·2. $C_{20}H_{22}Cl_3N_4O_9Rh$ requires C, 33·1; H, 4·0; N, 7·7; Cl, 14·6%). *trans*-$[Rh(py)_4Cl(OH)]ClO_4,H_2O$ was obtained by neutralisation of *trans*-$[Rh(py)_4Cl(OH_2)](ClO_4),H_2O$ with sodium hydroxide (Found: C, 40·7; H, 3·9; N, 9·4; Cl, 13·0. $C_{20}H_{23}Cl_2N_4O_6Rh$ requires C, 40·8; H, 3·9; N, 9·5; Cl, 12·1%).

trans-*Bromochlorotetra(pyridine)rhodium*(III) *Tetrafluoroborate*, trans-$[Rh(py)_4BrCl]BF_4$.—A solution of *trans*-$[Rh(py)_4Br(OH_2)](ClO_4)_2$ (0·15 g) was boiled with 6M-hydrochloric acid (20 ml) for 1 h. Concentration followed by addition of HBF_4 afforded orange needles of the product which was recrystallised from water; yield 0·07 g, ν(Rh–Cl) 350 cm^{-1}, $\lambda_{max.}$ 422 nm (ε 110) (Found: C, 38·6; H, 2·9; N, 9·3; Br, 12·9; Cl, 5·8. $C_{20}H_{20}BBrClF_4N_4Rh$ requires C, 38·7; H, 3·2; N, 9·0; Br, 12·9; Cl, 5·7%).

trans-*Diazidotetra(pyridine)rhodium*(III) *Azide Pentahydrate*, trans-$[Rh(py)_4(N_3)_2]N_3,5H_2O$.* A solution of compound (I) (0·5 g) in water (20 ml) containing sodium azide (0·13 g) was refluxed for 30 min. The orange solution was cooled and filtered; addition of sodium azide (4 g) gave yellow needles of the product, (0·25 g), Λ_E (10^{-3}M solution in water at 25°) = 73 Ω^{-1} mol^{-1} cm^2 (Found: C, 38·0; H, 5·1; N, 28·9. $C_{20}H_{30}N_{13}O_5Rh$ requires C, 37·8; H, 4·8; N, 28·7%). The tetrafluoroborate salt, *trans*-$[Rh(py)_4(N_3)_2]BF_4$ was prepared by addition of $NaBF_4$ instead of NaN_3 to the orange solution above (Found: C, 40·5; H, 3·5; N, 23·5. $C_{20}H_{20}BF_4N_6Rh$ requires C, 40·7; H, 3·4; N, 23·7%).

* All these complexes **explode violently** when heated.

[32] F. Basolo and G. Hammaker, *Inorg. Chem.*, 1962, **1**, 1.

[33] K. Hofmann, 'Imidazole and its Derivatives, Part I,' Interscience, 1953, p. 119, and references therein.

[34] C. E. Hazeldine, F. L. Pyman, and J. Winchester, *J. Chem. Soc.*, 1924, 1431.

[35] F. L. Pyman, *J. Chem. Soc.*, 1922, **121**, 2616.

1,2,6-*Triazidotri(pyridine)rhodium*(III), 1,2,6-$[Rh(py)_3(N_3)_3]$.*—To an aqueous solution containing compound (I) (0·5 g) and NaN_3 (0·4 g) was added $NaBH_4$ (1·0 mg). This resulted in the formation of an orange-yellow precipitate which was filtered off and recrystallised from acetonitrile to give deep orange prisms, (0·3 g), ν(N≡N) 2008 and 2030 cm^{-1} (Found: C, 38·7; H, 3·2; N, 36·0. $C_{15}H_{15}N_{12}Rh$ requires C, 38·6; H, 3·2; N, 36·0%). The 4-methylpyridine derivative was prepared in the same way starting from *trans*-$[Rh(4\text{-methylpyridine})_4Cl_2]Cl$: in this case the product was recrystallised from methanol (Found: C, 42·7; H, 4·2; N, 33·3. $C_{18}H_{21}N_{12}Rh$ requires C, 42·5; H, 4·2; N, 33·1%).

Tetraethylammonium Tetra-azidodi(pyridine)rhodate(III), $(NEt_4)[Rh(py)_2(N_3)_4]$.*—To a hot solution of compound (I) (0·6 g) in 60% aqueous ethanol (30 ml) was added NaN_3 (2 g) and then $NaBH_4$ (1·0 mg). The hot solution was filtered and then set aside overnight. Addition of NEt_4Cl (0·5 g) to this solution resulted in the precipitation of the product as a bright yellow solid which was filtered off and washed with water; it was recrystallised from water; yield 0·15 g, ν(N≡N) 2015 cm^{-1} (Found: C, 38·5; H, 5·3; N, 37·3. $C_{18}H_{30}N_{11}Rh$ requires C, 38·6; H, 5·4; N, 37·6%).

Halogenobis(isocyanato)tris(pyridine)rhodium(III), $[Rh(py)_3(NCO)_2X]$ (X = Cl *or* Br).—A solution of *trans*-$[Rh(py)_4X_2]X,5H_2O$ (0·001 mol) was heated to 50° with sodium cyanate for 30 min. (The same product was obtained using 0·002 mol and 0·01 mol of NaCNO). Yellow platelets (X = Cl) or orange-yellow crystals (X = Br) were formed which were filtered off, washed with water and ethanol and dried *in vacuo* over concentrated sulphuric acid [Found: (X = Cl): C, 44·5; H, 3·4; N, 15·1; Cl, 7·6. $C_{17}H_{15}ClN_5O_2Rh$ requires C, 44·4; H, 3·3; N, 15·2; Cl, 7·7%. Found (X = Br): C, 40·0; H, 3·0; N, 13·9. $C_{17}H_{15}BrN_5O_2Rh$ requires C, 40·5; H, 3·0; N, 13·9%].

Trinitrotris(pyridine)rhodium(III), $[Rh(py)_3(NO_2)_3]$.—To a warm solution of compound (I) (0·5 g) and $NaNO_2$ (2 g) in 30% aqueous ethanol was added $NaBH_4$ (1·0 mg). This resulted in the immediate precipitation of white crystals which were filtered off and washed with water and ether; yield 0·25 g (Found: C, 37·9; H, 3·1; N, 17·2. $C_{15}H_{15}N_6O_6Rh$ requires C, 37·7; H, 3·2; N, 17·6%).

Chloropentakis(N-methylimidazole)rhodium(III), $[Rh(miz)_5Cl]^{2+}X_2$ (X = ClO_4 *or* BF_4).—A solution containing rhodium trichloride (0·25 g) and miz (0·5 g) in 30% aqueous ethanol was heated under reflux for 15 min. The yellow solution was filtered, concentrated, and sodium perchlorate was added to it. The mixture was set aside overnight at 5° after which the pale yellow crystals were filtered off and recrystallised from methanol containing a little water; yield 0·51 g, $\lambda_{max.}$ 350 nm, ε 103; Λ = 154 Ω^{-1} mol^{-1} cm^2 (in nitromethane at 25 °C, *ca.* 1 × 10^{-3}M-solution) (Found: C, 32·3; H, 4·0; N, 18·6; Cl, 14·5. $C_{20}H_{30}N_{10}Cl_3O_8Rh$ requires C, 32·1; H, 4·0; N, 18·7; Cl, 14·3%). The tetrafluoroborate salt was obtained by addition of HBF_4 instead of $NaClO_4$ to the above solution. Yellow cubic crystals were obtained on recrystallisation from water; $\lambda_{max.}$ 350 nm (ε 100); Λ = 150 Ω^{-1} mol^{-1} cm^2 (in nitromethane at 25 °C, *ca.* 1 × 10^{-3}M-solution) (Found: C, 33·2; H, 3·9; N, 18·9. $C_{20}H_{30}N_{10}B_2ClF_8Rh$ requires C, 33·5; H, 4·2; N, 19·6%).

Bromopentakis(N-methylimidazole)rhodium(III) *Perchlorate* $[Rh(miz)_5Br](ClO_4)_2$.—The preparation was exactly analogous to that of the chloro-complex, except that the starting material is rhodium tribromide; $\lambda_{max.}$ 370nm (ε 111); Λ = 146 Ω^{-1} mol^{-1} cm^2 (in nitromethane at 25 °C, *ca.* 1 × 10^{-3}M-solution) (Found: C, 30·4; H, 3·7; N, 17·5; Br, 9·9; Cl, 8·8. $C_{20}H_{30}N_{10}BrCl_2O_8Rh$ requires C, 30·3; H, 3·8; N, 17·7; Br, 10·1; Cl, 9·0%).

Chloropenta-amminerhodium(III) *Chloride*, $[Rh(NH_3)_5Cl]Cl_2$.—To a warm solution of rhodium trichloride (0·5 g) and ammonium chloride (0·7 g) in water (8 ml) was added ethanol (2 ml). After 2—3 min, the solution was cooled to *ca.* 35 °C and ammonia solution (*d* 0·880) (3 ml) was added. The product crystallised out in at least 95% yield and the physical data agreed with those of authentic $[Rh(NH_3)_5Cl]Cl_2$.

trans-*Dichlorotetra*(N-*methylimidazole*)*rhodium*(III) *Chloride Trihydrate*, $[Rh(miz)_4Cl_2]Cl,3H_2O$.—A 50% aqueous ethanol solution of $[Rh(miz)_5Cl](ClO_4)_2$ (1 mol) and sodium chloride (*ca.* 150 mol) was refluxed in the absence of oxygen at 82 °C, the pH of the solution having been adjusted to *ca.* 3 by addition of concentrated hydrochloric acid. Concentration of the cooled solution gave yellow needle-like crystals of the product which were recrystallised from water–acetone. Physical and analytical data are given in Table 4.

* See previous footnote.

TABLE 4

Some properties of *N*-methylimidazole and substituted *N*-methylimidazole complexes of the type *trans*-$[RhL_4X_2]Y,xH_2O$

L	X	Y	*x*	$\lambda_{max.}$	ε	A_{H_2O} *	$A_{CH_3NO_2}$ *	Formula	Found (%) C	H	N	Cl/Br	Required (%) C	H	N	Cl/Br	
5-Nitro-*N*-methylimidazole	Cl	Cl	2	†		105·6	37·2	$C_{16}H_{24}N_{12}O_{10}Cl_3Rh$	25·5	2·9	21·9	14·5	25·5	2·7	22·3	14·1	*a*
5-Nitro-*N*-methylimidazole	Cl	Cl	4	†				$C_{16}H_{28}N_{12}O_{12}Cl_3Rh$	24·7	2·6	21·3	13·4	24·3	2·6	21·3	13·5	*a*
5-Nitro-*N*-methylimidazole	Cl	ClO_4	0	†			84·3	$C_{16}H_{20}N_{12}O_{12}Cl_3Rh$	24·3	2·8	21·2		24·7	2·6	21·6		*b*
5-Nitro-*N*-methylimidazole	Br	Br	1	439			33·4	$C_{16}H_{22}N_{12}O_9Br_3Rh$	22·0	2·8	16·8		22·1	2·6	19·3		*c*
5-Chloro-*N*-methylimidazole	Cl	Cl	2	409	81	91·8		$C_{16}H_{24}N_8O_2Cl_7Rh$	26·7	3·3	15·8	34·9	27·0	3·4	15·7	34·8	*d*
5-Chloro-*N*-methylimidazole	Br	Br	2	438	131	112·7		$C_{16}H_{24}N_8O_2Cl_4Br_3Rh$	22·5	2·3	13·4		22·8	2·4	13·3		*b*
N-Methylimidazole	Cl	Cl	3	410	71		79·5	$C_{16}H_{30}N_8O_3Cl_3Rh$	32·4	4·2	18·6		32·5	4·1	18·9		*a*
N-Methylimidazole	Br	Br	1	439	124		80·2	$C_{16}H_{26}N_8OBr_3Rh$	28·1	3·6	16·2		27·9	3·5	16·3		*b*

Recrystallised from: [a] Water–acetone. [b] Water. [c] Water–dimethyl sulphoxide. [d] Water–ethanol.

* Conductivity (Ω^{-1} cm^2 mol^{-1}) of *ca.* 10^{-3}M solutions at 25 °C. † Obscured by charge transfer bands.

trans-*Dibromotetra*(N-*methylimidazole*)*rhodium*(III) *Bromide Monohydrate*, $[Rh(miz)_4Br_2]Br,H_2O$.—This complex may be prepared as above, substituting sodium bromide for sodium chloride. There again appears to be a critical temperature for reaction (*ca.* 73 °C), and the reaction is completely inhibited by oxygen. The orange-yellow crystals were recrystallised from water. Physical data are given in Table 4.

Another preparative route involves ethanol-catalysed substitution of $[Rh(miz)_4Cl_2]Cl$ by bromide ion.

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