Rhodium(III) Complexes containing Unidentate Amines

By **Steve P. Dagnall, Martin P. Hancock,** and **Brian T. Heaton,**[*,†] Chemical Laboratory, University of Kent, Canterbury CT2 7NH

D. Huw Vaughan, Chemistry Department, Paisley College of Technology, Paisley PA1 2BE

Convenient syntheses of $[Rh(NRH_2)_5X]^{2+}$ (R = Me, Et, Pr^n, Bu^n, or Bu^i; X = Cl or Br), $trans$-$[Rh(NR'H_2)_4Cl_2]^+$ (R' = Pr^i, cyclohexyl, or Ph), and $trans$-$[Rh(pyr)_4Cl_2]^+$ (pyr = pyrrolidine) are reported and $[Rh(NRH_2)_5Cl]^{2+}$ is shown to be a convenient starting material for the synthesis of $trans$-$[Rh(NRH_2)_4Cl_2]^+$. Polarographic half-wave reduction potentials are reported together with physical and spectroscopic properties. The rate of exchange of amino-protons in $trans$-$[Rh(NMeH_2)_4Cl_2]^+$ and the rate constants and activation parameters for the substitution of chloride by bromide in $[Rh(NRH_2)_5Cl]^{2+}$ and $trans$-$[Rh(NRH_2)_4Cl_2]^+$ (R = Me, Et, or Pr^n) have been determined and are compared with data on related complexes of Rh^{III}, Co^{III}, and Cr^{III}.

ALTHOUGH rhodium(III) ammine complexes of the types $[Rh(NH_3)_5X]^{2+}$, $trans$-$[Rh(NH_3)_4X_2]^+$, and cis-$[Rh(NH_3)_4X_2]^+$ (X = Cl or Br) are readily prepared,[1-5] there are few reports of the synthesis of analogues containing unidentate primary or secondary amines. Shubochkina *et al.*[6] prepared pentakis(allylamine)chloro-rhodium(III) chloride by reaction of dry ' rhodium chloride ' with allylamine, whilst Sawai and Hirai[7] reported the synthesis of the same complex and $[Rh(NPr^nH_2)_5Cl]Cl_2$ by the reaction of an excess of the amine with an ethanolic solution of $RhCl_3 \cdot 3H_2O$. The preparation of cis-$[Rh(NRH_2)_4Cl_2]X$ (R = Me, Et, Pr^n,

or allyl; X = Cl or NO_3) and $trans$-$[Rh(NRH_2)_4Cl_2]^+$ (R = Me or Et), by titration of an acidic aqueous methanol solution of chlororhodate(III) species (prepared by electrolytic dissolution of rhodium metal in hydrochloric acid) with the appropriate amine, has been described[6] and more recently the synthesis of $trans$-$[Rh(NRH_2)_4XY]^+$ (R = Me or Et; X,Y = Cl, Br, or I) has been reported.[8,9] Rhodium(III) complexes containing aziridine, $[Rh(az)_5Cl]^{2+}$ and $[Rh(az)_4X_2]^+$ (az = aziridine; X = Cl or Br), have also been described.[10]

As part of a general study of the chemical and kinetic

† *Present address:* Lash Miller Laboratories, 80 St. George St., Toronto, Canada, M5S 1A1.

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properties of rhodium complexes containing nitrogen-donor ligands, we now describe convenient procedures for the preparation of $[Rh(NRH_2)_5X]^{2+}$, trans-$[Rh(NRH_2)_4X_2]^+$, trans-$[Rh(NR'H_2)_4Cl_2]^+$, and trans-$[Rh(pyr)_4Cl_2]^+$ (R = primary alkyl; R' = Pr^i, C_6H_{11}, or Ph; X = Cl or Br; pyr = pyrrolidine). Infrared, Raman, electronic, and ^1H n.m.r. data are reported, together with the polarographic half-wave reduction potentials of $[Rh(NRH_2)_5X]^{2+}$ and trans-$[Rh(NRH_2)_4Cl_2]^+$ (R = Me, Et, Pr^n, Bu^n, or Bu^i; X = Cl or Br). The rate constants and activation parameters for the replacement of chloride by bromide in $[Rh(NRH_2)_5Cl]^{2+}$ and

ing amines, both these routes give only trans-$[RhL_4Cl_2]^+$ [L = NPr^{i}H$_2$, pyr, N(C_6H_{11})H$_2$, or NPhH$_2$]. Related results have been obtained in the preparation of cobalt-(III) amine complexes.[16a,c,20]

The synthesis of trans-$[Rh(NRH_2)_4Cl_2]^+$ (R = Me or Et) from an electrochemically generated chlororhodate-(III) species has been described,[6] but replacement of this rather inconvenient starting material with $RhCl_3 \cdot 3H_2O$ did not give tetrakis(alkylamine) complexes. However, complexes of the type trans-$[Rh(NRH_2)_4Cl_2]^+$ (R = Me, Et, Pr^n, Bu^n, or Bu^i) were readily prepared by reaction of an aqueous ethanolic solution of $[Rh(NRH_2)_5Cl]Cl_2$

TABLE 1

Analytical and conductivity data for pentakis(amine)halogeno- and trans-tetrakis(amine)dihalogeno-rhodium (III) complexes

	Found				Calc.				Λ ^{a}
Complex	C	H	N	Halogen	C	H	N	Halogen	S cm² mol⁻¹
$[Rh(NMeH_2)_5Cl]Cl_2$	16.3	6.9	19.3	29.2	16.5	6.9	19.2	29.2	197
$[Rh(NEtH_2)_5Cl]Cl_2 \cdot 0.5H_2O$	27.5	8.0	16.3	24.0	27.1	8.0	15.8	24.0	189
$[Rh(NPr^nH_2)_5Cl]Cl_2$	35.9	8.8	14.1		35.7	9.0	13.9		183
$[Rh(NBu^nH_2)_5Cl]Cl_2$	41.4	9.7	12.1	18.9	41.8	9.6	12.2	18.5	184
$[Rh(NBu^iH_2)_5Cl]Cl_2 \cdot H_2O$	40.4	9.8	11.6		40.5	9.7	11.8		169
$[Rh(NMeH_2)_5Br]Br_2$	11.9	5.2	14.4		12.1	5.1	14.1		234
$[Rh(NEtH_2)_5Br]Br_2$	21.6	6.6	12.6		21.1	6.2	12.3		193
$[Rh(NPr^nH_2)_5Br]Br_2$	27.8	6.8	10.9		28.2	7.1	11.0		195
$[Rh(NBu^nH_2)_5Br]Br_2$	33.4	8.4	9.6 [b]		33.9	7.8	9.9		195
$[Rh(NBu^iH_2)_5Br]Br_2 \cdot H_2O$	33.3	8.4	9.7 [c]		33.1	7.9	9.6		187
trans-$[Rh(NPr^iH_2)_4Cl_2]Cl$	32.6	7.9	12.5		32.3	8.1	12.6		84
trans-$[Rh(NPr^iH_2)_4Cl_2][ClO_4]$	28.7	7.5	11.3		28.3	7.1	11.0		64 [d]
trans-$[Rh(pyr)_4Cl_2]Cl$	40.1	7.8	11.6		38.9	7.4	11.3		70 [d]
trans-$[Rh(pyr)_4Cl_2][ClO_4]$	34.6	6.8	10.1		34.4	6.5	10.0		
trans-$[Rh\{N(C_6H_{11})H_2\}_4Cl_2]Cl$	47.8	8.9	9.2		47.6	8.7	9.2		69 [d]
trans-$[Rh(NPhH_2)_4Cl_2]Cl$	49.5	5.0	9.5		49.5	4.9	9.6		68 [d]
trans-$[Rh(NMeH_2)_4Cl_2]Cl$	14.1	6.1	16.6	31.8	14.4	6.0	16.8	31.9	84
trans-$[Rh(NEtH_2)_4Cl_2][NO_3]$	23.4	6.8	17.1		23.1	6.8	16.8		85
trans-$[Rh(NPr^nH_2)_4Cl_2]Cl$	32.4	7.7	12.5		32.3	8.1	12.6		100
trans-$[Rh(NBu^nH_2)_4Cl_2]Cl$	38.8	9.1	11.3		38.3	8.8	11.2		75
trans-$[Rh(NBu^iH_2)_4Cl_2]Cl \cdot H_2O$	37.1	8.7	10.9		37.0	8.9	10.8		84
trans-$[Rh(NMeH_2)_4Br_2]Br$	10.0	4.6	11.4	51.5	10.3	4.3	12.0	51.4	

^{a} Molar conductivity calculated from conductivity of ca. 10^{-3} mol dm⁻³ aqueous solutions at 25 °C. [b,c] Absence and presence, respectively, of crystal water confirmed by i.r. spectra (Nujol mulls; 400—4 000 cm⁻¹). [d] In methanol.

trans-$[Rh(NRH_2)_4Cl_2]^+$ (R = Me, Et, or Pr^n) have been measured and are compared with data obtained for other aminehalogenorhodium(III) complexes,[4,11—15] and with data for the aquation of $[M(NRH_2)_5Cl]^{2+}$ (M = Co [16,17] or Cr [18]).

RESULTS AND DISCUSSION

Syntheses and Spectroscopic Properties.—Using a procedure similar to that described for the preparation of $[Rh(NH_3)_5Cl]Cl_2$,[19] we found that $[Rh(NRH_2)_5X]X_2$ (R = Me, Et, Pr^n, Bu^n, or Bu^i; X = Cl or Br) could be obtained in high yields. The chloro-complexes are also formed on reaction of excess of free amine with an ethanolic solution of $RhCl_3 \cdot 3H_2O$ but this procedure is generally less convenient. With more sterically demand-

under reflux with excess of sodium chloride. When R = Me or Et, higher yields of the tetrakis(alkylamine) complex were obtained using a procedure analogous to that employed for the preparation of trans-$[Rh(NH_3)_4Cl_2]^+$;[4] this method, however, was unsuccessful when R = Pr^n, Bu^n, or Bu^i.

The formulations of the above complexes are supported by analytical and conductivity data (Table 1), and by spectroscopic measurements. The electronic spectra of the pentakis- and tetrakis-(amine)rhodium(III) complexes are reported in Table 2, together with those of some related chromophores. As found for $[Co(NRH_2)_5Cl]^{2+}$ (R = H or Me),[16a,b] the d–d bands for

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$[Rh(NRH_2)_5Cl]^{2+}$ shift to lower energy on going from R = H to a primary alkyl and a similar effect was observed for the tetrakis(amine) complexes.

Comparison of the Raman and far-i.r. spectra of the chloro- and bromo-complexes of $[Rh(NRH_2)_5X]X_2$ containing a given alkylamine allows assignment of $\nu(Rh-X)$ (Table 2), which is found to vary considerably (X = Cl, 290—343; X = Br, 170—217 cm^{-1}) on changing the amine, but there is no systematic trend. The frequency

is slower and, in this case, the ^1H n.m.r. spectrum (pD $ca.$ 7) consists of a sharp triplet $[\tau$ 7.58, $^3J(H_2NCH_3)$ 6.3 Hz]. The second-order rate constant for amino-proton exchange $[(3.24 \pm 0.16) \times 10^3$ dm^3 mol^{-1} s$^{-1}]$ for $trans$-$[Rh(NMeH_2)_4Cl_2]^+$ in D_2O (pD $ca.$ 7.4) at 295 K, obtained using the usual rate law [22,23] and a value of 14.82 for the pK_a of D_2O at 295 K,[24] is approximately two orders of magnitude less than those found for $[Rh(L-L)_3]^{3+}$ [L-L = ethylenediamine (en) or

Electronic-absorption spectra in aqueous solution and Raman (i.r. in parentheses) assignments (cm^{-1}) of $\nu(Rh-X)$ for complexes of the types $[RhL_5X]Y_2$ and $trans$-$[RhL_4X_2]Y$ (L = amine group; X = Cl or Br; Y = Cl, Br, ClO$_4$, or NO$_3$)

| | Absorption spectrum | | Assignment of $\nu(Rh-X)$ in |
Complex	$\lambda_{max.}/nm$	$\varepsilon_{max.}/dm^3$ mol^{-1} cm^{-1}	Raman (i.r.) spectrum
$[Rh(mim)_5Cl][BF_4]_2$ [a]	350,	100 [b]	292 (294)
$[Rh(NH_3)_5Cl]Cl_2$	349, 277	100, 103 [c]	276 (274 or 282) [d]
$[Rh(NMeH_2)_5Cl]Cl_2$	358, 285	118, 146	343 (343)
$[Rh(NEtH_2)_5Cl]Cl_2 \cdot 0.5H_2O$	358, 286	144, 185	290 (292)
$[Rh(NPr^nH_2)_5Cl]Cl_2$	359, 286	168, 212	320 (320)
$[Rh(NBu^nH_2)_5Cl]Cl_2$	360, 287	178, 229	312 (313)
$[Rh(NBu^iH_2)_5Cl]Cl_2 \cdot H_2O$	362, 289	158, 204	315 (314)
$[Rh(NH_3)_5Br]Br_2$	424 (sh), 359	25, 122 [c]	
$[Rh(NMeH_2)_5Br]Br_2$	435 (sh), 370	29, 140	214 (217)
$[Rh(NEtH_2)_5Br]Br_2$	438 (sh), 373	33, 165	185 (188)
$[Rh(NPr^nH_2)_5Br]Br_2$	442 (sh), 378	51, 185	183 (182)
$[Rh(NBu^nH_2)_5Br]Br_2$	446 (sh), 379	32, 173	172 (170)
$[Rh(NBu^iH_2)_5Br]Br_2 \cdot H_2O$	447 (sh), 380	35, 172	171 (172)
$trans$-$[Rh(en)_2Cl_2][NO_3]$ [e]	406, 286	75, 130 [f]	309 [g]
$trans$-$[Rh(NH_3)_4Cl_2]Cl$	415, 293	74, 85 [h]	310
$trans$-$[Rh(NMeH_2)_4Cl_2]Cl$	424, 302	86, 143	307
	420, 300	78, 120 [i]	
$trans$-$[Rh(NEtH_2)_4Cl_2][NO_3]$	425, 302	104, 191	301
$trans$-$[Rh(NEtH_2)_4Cl_2]Cl$	420, 300	78, 120 [i]	
$trans$-$[Rh(NPr^nH_2)_4Cl_2]Cl$	426, 304	98, 194	300
$trans$-$[Rh(NBu^nH_2)_4Cl_2]Cl$ [j]	426, 305 (sh)	112, 235	303
$trans$-$[Rh(NBu^iH_2)_4Cl_2]Cl \cdot H_2O$ [j]	426, 300 (sh)	118, 308	303
$trans$-$[Rh(NPr^iH_2)_4Cl_2]Cl$ [j]	430, 311	89, 181	299
$trans$-$[Rh(pyr)_4Cl_2]Cl$ [k]	439, 350 (sh), 320	79, 116, 185	289
$trans$-$[Rh\{N(C_6H_{11})H_2\}_4Cl_2]Cl$ [l]	428, 305 (sh)	110, 320	302
$trans$-$[Rh(NPhH_2)_4Cl_2]Cl$ [j]	440, 279	174, $ca.$ 10 000	
$trans$-$[Rh(NH_3)_4Br_2]Br$	441, $ca.$ 280 (sh)	111, 2 700 [h]	
$trans$-$[Rh(NMeH_2)_4Br_2]Br$	449, 281	129, 3 210	

[a] mim = 1-Methylimidazole. [b] Ref. 19. [c] C. K. Jørgensen, $Acta$ $Chem.$ $Scand.$, 1956, 10, 500. [d] Ref. 21. [e] en = Ethylenediamine. [f] Ref. 3. [g] Ref. 13. [h] Ref. 4. [i] Ref. 6. [j-l] Solvent for absorption spectroscopy: ethanol, methanol, and water-ethanol (1 : 4) respectively.

of the symmetric Rh-Cl stretching vibration in $trans$-$[RhL_4Cl_2]Y$ (L = NH$_3$, primary alkylamine, cyclohexylamine, or pyr; Y = Cl, ClO$_4$, or NO$_3$), however, changes very little with L or Y.

The ^1H n.m.r. spectra of the chloropentakis- and $trans$-dichlorotetrakis-(amine) complexes are generally uninformative except in the case of the methylamine complexes. The spectrum of $[Rh(NMeH_2)_5Cl]Cl_2$ in acidic D$_2$O (pD $ca.$ 2) shows two overlapping triplets at τ 7.59 and 7.70 $[^3J(H_2NCH_3)$ 6.6 Hz] due to the methyl groups cis and $trans$ to chloride respectively; at pD $ca.$ 7 both these resonances collapse to singlets because of fast exchange of the amino-protons with solvent. In keeping with the reduced charge on the cation,[22] the rate of amino-proton exchange in $trans$-$[Rh(NMeH_2)_4Cl_2]^+$

$2NH_3]$.[25] It was unfortunately not possible to obtain accurate rate data for amino-proton exchange in $[Rh(NMeH_2)_5Cl]^{2+}$ because the two methyl resonances overlap in the ^1H n.m.r. spectrum. Nevertheless, the spectra clearly show that amino-protons $trans$ to chloride exchange at a much faster rate than those cis to chloride, as found for $[Co(NMeH_2)_5Cl]^{2+}$.[16b,c]

Polarographic-reduction Behaviour.—The relation between polarographic half-wave potentials $(E_{\frac{1}{2}})$ and the energy of the first ligand-field absorption bond $(\nu_{max.})$ is now clearly established for homologous series of chromium(III), cobalt(III), and rhodium(III) complexes.[13,26-28] The values of $E_{\frac{1}{2}}$ and $\nu_{max.}$ for $[Rh(NRH_2)_5X]^{2+}$, $trans$-$[Rh(NRH_2)_4Cl_2]^+$ (R = H or primary alkyl; X = Cl or Br), and some related complexes are in Table 3 and, although the variation in $E_{\frac{1}{2}}$ pro-

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duced by changing R = H to a primary alkyl is much more pronounced for the pentakis complexes, the trends in $E_{\frac{1}{2}}$ for both series of complexes are in the expected direction.

Kinetics of Replacement of Chloride by Bromide in

TABLE 3

Polarographic half-wave potentials and longest-wavelength ligand-field band energies for $[Rh(NRH_2)_5X]^{2+}$, *trans*-$[Rh(NRH_2)_4X_2]^+$ (R = H or primary alkyl; X = Cl or Br), and some related complexes in aqueous solution

Complex	$-E_{\frac{1}{2}}/V$ *versus* s.c.e.	$10^{-3}\nu_{max.}/$ cm^{-1}
$[Rh(mim)_5Cl]^{2+}$	0.57 [a]	28.6
$[Rh(NH_3)_5Cl]^{2+}$	0.94 [b]	28.7
$[Rh(NMeH_2)_5Cl]^{2+}$	0.70	27.9
$[Rh(NEtH_2)_5Cl]^{2+}$	0.74	27.9
$[Rh(NPr^nH_2)_5Cl]^{2+}$	0.73	27.9
$[Rh(NBu^nH_2)_5Cl]^{2+}$	0.74	27.8
$[Rh(NBu^iH_2)_5Cl]^{2+}$	0.69	27.6
$[Rh(NMeH_2)_5Br]^{2+}$	0.58	23.0
$[Rh(NEtH_2)_5Br]^{2+}$	0.60	22.8
$[Rh(NPr^nH_2)_5Br]^{2+}$	0.61	22.6
trans-$[Rh(en)_2Cl_2]^+$	0.70 [a]	24.6
trans-$[Rh(NH_3)_4Cl_2]^+$	0.57	24.1
trans-$[Rh(NMeH_2)_4Cl_2]^+$	0.53	23.6
trans-$[Rh(NEtH_2)_4Cl_2]^+$	0.49	23.5
trans-$[Rh(NPr^nH_2)_4Cl_2]^+$	0.53	23.5
trans-$[Rh(NBu^nH_2)_4Cl_2]^+$	0.56 [c]	23.5
trans-$[Rh(NBu^iH_2)_4Cl_2]^+$	0.51 [c]	23.5

[a] A. W. Addison, R. D. Gillard, and D. H. Vaughan, *J.C.S. Dalton*, 1973, 1187. [b] Ref. 29. [c] In water–ethanol (4 : 1).
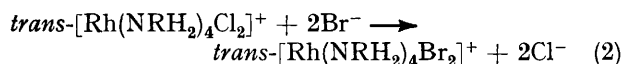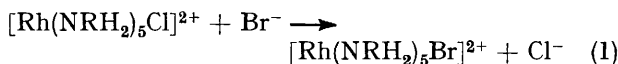
TABLE 4

Kinetic data for the reactions $[Rh(NRH_2)_5Cl]^{2+} + Br^- \longrightarrow$ $[Rh(NRH_2)_5Br]^{2+} + Cl^-$ in water at $I = 0.2$ mol dm^{-3} with Na[ClO$_4$] and [Rh] = *ca.* 10^{-3} mol dm^{-3}

R	$\dfrac{T}{K}$	$\dfrac{[Br^-]\,*}{mol\ dm^{-3}}$	$\dfrac{10^5k}{s^{-1}}$
Me	354.5	0.2	1.80
	358	0.2	3.27
	363	0.2	5.44
Et	334.5	0.05	0.65
		0.1	0.63
		0.2	0.63
	343	0.05	1.70
		0.1	1.67
		0.2	1.69, 1.67
	344	0.2	1.81, 1.82
	353	0.2	4.50
	355	0.2	5.77
	359.5	0.2	8.05, 8.26
Pr^n	337	0.1	1.03
		0.2	1.00
	348	0.1	3.40
		0.2	3.42
	354	0.2	5.92

* As sodium salt.

$[Rh(NRH_2)_5Cl]^{2+}$ *and* trans-$[Rh(NRH_2)_4Cl_2]^+$ (R = Me, Et, *or* Pr^n).—Reactions (1) and (2) go to completion

$$[Rh(NRH_2)_5Cl]^{2+} + Br^- \longrightarrow$$
$$[Rh(NRH_2)_5Br]^{2+} + Cl^- \quad (1)$$

$$\textit{trans}\text{-}[Rh(NRH_2)_4Cl_2]^+ + 2Br^- \longrightarrow$$
$$\textit{trans}\text{-}[Rh(NRH_2)_4Br_2]^+ + 2Cl^- \quad (2)$$

under the conditions employed and there was no evidence for *trans* $\longrightarrow$ *cis* isomerisation in (2) (see Experimental section). The observed rates were independent of bromide concentration (Tables 4 and 5)

and no intermediates were observed. These results parallel those obtained in previous studies.[4,11-15]

The observed orders of rate constants for the reactions of $[Rh(NRH_2)_5Cl]^{2+}$ and *trans*-$[Rh(NRH_2)_4Cl_2]^+$ with bromide at 353 K are Pr^n > Et > H > Me and H > Pr^n > Et > Me respectively, whilst the activation enthalpies and entropies for both series are Me > Pr^n ≈ Et ≈ H (Tables 6 and 7). Qualitatively, therefore, the

TABLE 5

Kinetic data for the reactions *trans*-$[Rh(NRH_2)_4Cl_2]^+$ + $2Br^- \longrightarrow$ *trans*-$[Rh(NRH_2)_4Br_2]^+$ + $2Cl^-$ in water at $I = 0.2$ mol dm^{-3} with Na[ClO$_4$] and [Rh] = *ca.* 10^{-3} mol dm^{-3}

R	$\dfrac{T}{K}$	$\dfrac{[Br^-]\,*}{mol\ dm^{-3}}$	$\dfrac{10^5k}{s^{-1}}$
Me	345.8	0.2	0.75
	347	0.2	0.97
	354.5	0.2	2.60
	359	0.2	3.78
Et	333	0.1	0.57
		0.2	0.49, 0.59
	343	0.05	1.67
		0.2	1.63, 1.42
	354	0.05	4.84
		0.1	5.30
		0.2	5.13, 5.62
Pr^n	337	0.1	0.61
	348	0.1	3.58
		0.2	2.82, 3.20
	354	0.1	8.38
		0.2	6.20, 6.83
	361	0.1	16.9
		0.2	15.2

* As sodium salt.

TABLE 6

Summary of kinetic parameters [a] for the reactions $[Rh(NRH_2)_5Cl]^{2+} + Br^- \longrightarrow [Rh(NRH_2)_5Br]^{2+} + Cl^-$ in aqueous solution

R	$\dfrac{10^5k \text{ at } 353\ K}{s^{-1}}$	$\dfrac{\Delta H^{\ddagger}}{kcal\ mol^{-1}}$	$\dfrac{\Delta S^{\ddagger}}{cal\ K^{-1}\ mol^{-1}}$
H [b]	3.11	24.2 ± 0.3	−11.1 ± 0.8
Me	1.64 [c]	32.1 ± 4.6	10.2 ± 12.9
Et	4.50	24.1 ± 0.7	−11 ± 2
Pr^n	5.40 [c]	23.7 ± 1.0	−11 ± 3

[a] Uncertainties are standard deviations; 1 cal = 4.184 J. [b] Data from ref.11; $I = 0.2$ mol dm^{-3} with [NH$_4$]Br. [c] Interpolated from data for other temperatures.

TABLE 7

Summary of kinetic parameters [a] for the reactions *trans*-$[Rh(NRH_2)_4Cl_2]^+$ + $2Br^- \longrightarrow$ *trans*-$[Rh(NRH_2)_4Br_2]^+$ + $2Cl^-$ in aqueous solution

R	$\dfrac{10^5k \text{ at } 353\ K}{s^{-1}}$	$\dfrac{\Delta H^{\ddagger}}{kcal\ mol^{-1}}$	$\dfrac{\Delta S^{\ddagger}}{cal\ K^{-1}\ mol^{-1}}$
H [b]	8.2 [c]	24.11 ± 0.39	−9.2 ± 1.1
Me	2.0 [c]	29.2 ± 1.0	2.3 ± 2.3
Et	4.59 [c]	24.5 ± 0.7	−9.4 ± 2.1
Pr^n	5.75 [c]	24.9 ± 3.3	−7.8 ± 9.3

[a] Uncertainties are standard deviations. [b] Data from ref. 4; $I = 0.05$–0.01 mol dm^{-3} with NaBr. [c] Interpolated from data for other temperatures.

behaviour of these rhodium(III) complexes resembles that [18] of $[Cr(NRH_2)_5Cl]^{2+}$ much more closely than that of the cobalt(III) analogues,[16,17] suggesting that bond making plays a more important role than bond

[29] J. B. Willis, *J. Amer. Chem. Soc.*, 1944, **66**, 1067.

breaking in transition-state formation.[30,31] This is consistent with previous studies of the anation [32] and water exchange [33] of $[Rh(NH_3)_5(OH_2)]^{3+}$ which lead to the conclusion that the kinetic behaviour in these rhodium-(III) reactions is best accounted for by an associative interchange (I_a) [30] mechanism.

EXPERIMENTAL

The instrumentation used in this work has been described previously.[13,15] Elemental microanalyses were by the University of Kent microanalytical laboratory and by the Microanalytical Laboratory, H. C. Ørsted Institute, University of Copenhagen.

Preparation of Complexes.—Pentakis(alkylamine)chlororhodium(III) *dichloride*, $[Rh(NRH_2)_5Cl]Cl_2 \cdot nH_2O$ (R = Me, Et, Pr^n, Bu^n, *or* Bu^i). The basic procedure for the synthesis of these complexes was the same and only the synthesis of the methylamine complex is described in detail. Yields were *ca.* 50—80%.

R = Me, n = 0. Rhodium trichloride trihydrate (2.0 g, 7.6 mmol) was dissolved in a solution of methylammonium chloride (3.5 g, 52 mmol) in water (20 cm³). Ethanol (5 cm³) was added and the solution was warmed to 323 K A 40% aqueous solution of methylamine (8 cm³, *ca.* 100 mmol) was then added to the vigorously stirred deep red solution which rapidly became bright yellow and yellow crystals were deposited. After cooling in ice, the crystals were filtered off, washed with ethanol, and dried in air. Recrystallisation from the minimum volume of 1 mol dm⁻³ HCl (*ca.* 100 cm³) gave the product as pale yellow crystals which were washed with 4 mol dm⁻³ HCl and ethanol and dried *in vacuo*. Yield 2.27 g (82%).

For R = Pr^n, Bu^n, and Bu^i, aqueous ethanol (2 : 1, 4 : 3, and 1 : 1 respectively) was used for recrystallisation.

Pentakis(alkylamine)bromorhodium(III) *dibromide*, [Rh(NRH_2)_5Br]Br_2 \cdot nH_2O (R = Me, Et, Pr^n, Bu^n, *or* Bu^i). Two slightly different procedures were used: one employed commercial RhBr_3 \cdot 3H_2O and the other a solution of bromorhodate(III) species produced by treating commercial RhCl_3 \cdot 3H_2O with an excess of sodium bromide. The two methods gave comparable results and are described in full for the methyl- and ethyl-amine complexes, respectively. Yields were *ca.* 40—60%.

R = Me, n = 0. Rhodium tribromide trihydrate (0.20 g) was finely ground and suspended in a solution of methylammonium chloride (1.0 g) and NaBr (1.0 g) in water (8 cm³). Ethanol (2 cm³) was added and the mixture was warmed to *ca.* 323 K. A 25% (w/v) aqueous solution of methylamine (4 cm³) was added and, on shaking vigorously (*ca.* 5 min), the suspended RhBr_3 \cdot 3H_2O reacted to give a bright yellow solution which, on cooling in ice, gave a yellow precipitate. This was filtered off and recrystallised from the minimum volume of hot water to give the product as yellow crystals. Yield 0.12 g (48%).

R = Et, n = 0. A solution of bromorhodate(III) species was prepared by dissolving RhCl_3 \cdot 3H_2O (0.30 g) and NaBr (10.3 g) in a solution of ethylammonium bromide (2 g) in water (10 cm³), adding ethanol (5 cm³), and warming to *ca.* 313 K. Addition of an aqueous solution of ethylamine (70% w/v; 5 cm³) to the vigorously agitated mixture gave a cloudy yellow solution which on cooling gave yellow crystals. These were filtered off, recrystallised from hot

water containing a little NaBr, washed with aqueous ethanol (1 : 9), and dried *in vacuo*. Yield 0.26 g (40%). When R = Pr^n the product was recrystallised from water containing NaBr and for R = Bu^n and Bu^i aqueous ethanol (3 : 2 and 1 : 1 respectively) was used.

trans-*Tetrakis(amine)dichlororhodium*(III) *chloride or perchlorate*, trans-[RhL_4Cl_2]X (L = pyr, NPrH_2, N(C_6H_{11})H_2, *or* NPhH_2; X = Cl *or* ClO_4).

L = pyr, X = Cl. Pyrrolidine (4 cm³) was added to a solution of RhCl_3 \cdot 3H_2O (0.50 g) in absolute ethanol (65 cm³) at *ca.* 313 K. Cooling the resulting solution to 273 K gave orange-yellow crystals which were filtered off, washed with ethanol and diethyl ether, and dried *in vacuo*. Yield 0.45 g (48%).

L = pyr, X = ClO_4. Addition of a solution of Na-[ClO_4] \cdot H_2O (1.0 g) in water (5 cm³) to a solution of trans-[Rh(pyr)_4Cl_2]Cl (0.12 g) in aqueous methanol (3 : 7, 50 cm³) gave a yellow precipitate, which was filtered off, washed with water, and dried *in vacuo*. Yield 0.11 g (81%). Both this salt and the chloride (above) developed a distinct odour of free pyrrolidine on storage.

L = NPr^{i}H_2, X = Cl. This complex was prepared as for the chloride salt of the pyrrolidine complex (above), using RhCl_3 \cdot 3H_2O (0.50 g), absolute ethanol (12 cm³), and isopropylamine (3 cm³). The orange-yellow crystals were recrystallised from absolute ethanol, washed with cold ethanol and diethyl ether, and dried *in vacuo*. Yield 0.18 g (21%).

L = NPr^{i}H_2, X = ClO_4. The mother liquor from the preparation of the chloride salt was heated to give a clear solution and treated with a solution of Li[ClO_4] \cdot 3H_2O (0.5 g) in ethanol (5 cm³). The solution was evaporated to *ca.* 10 cm³, cooled in ice, and the product was filtered off and recrystallised as for the chloride salt (above). Yield 0.36 g (37%).

L = N(C_6H_{11})H_2, X = Cl. Rhodium trichloride trihydrate (0.50 g) was dissolved in a solution of cyclohexylammonium chloride (1.4 g) in aqueous ethanol (5 : 1, 12 cm³). The solution was warmed to *ca.* 323 K and addition of cyclohexylamine (2 cm³) gave an orange solution which deposited an orange-yellow solid on cooling. The product was filtered off, washed with ethanol, water, and finally methanol, and dried *in vacuo*. Yield 0.44 g (38%).

L = NPhH_2, X = Cl. Aniline (3 cm³) was added to a vigorously stirred solution of RhCl_3 \cdot 3H_2O (0.20 g) in ethanol (25 cm³) at *ca.* 313 K. Evaporation of the resulting yellow-brown solution gave an oil. Addition of water (30 cm³) followed by vigorous shaking and standing overnight gave yellow-brown needles which were filtered off and washed with diethyl ether. The product was then recrystallised from methanol by addition of diethyl ether, washed with diethyl ether, and dried *in vacuo*. Yield 0.20 g (45%).

trans-*Tetrakis(alkylamine)dichlororhodium*(III) *chloride or nitrate*, trans-[Rh(NRH_2)_4Cl_2]X \cdot nH_2O (R = Me, Et, Pr^n,Bu^n, *or* Bu^i; X = Cl *or* NO_3).

R = Me, X = Cl, n = 0. The highest yield was obtained by an adaptation of the method used for the preparation of trans-[Rh(NH_3)_4Cl_2]Cl.[4] Warming a mixture of [Rh-

[30] C. H. Langford and H. B. Gray, ' Ligand Substitution Processes,' Benjamin, New York, 1966, ch. 1.
[31] T. W. Swaddle, *Co-ordination Chem. Rev.*, 1974, **14**, 217.

[32] F. Monacelli, *Inorg. Chim. Acta*, 1968, **2**, 263; H. L. Bott, A. J. Poë, and K. Shaw, *Chem. Comm.*, 1968, 793; H. L. Bott, A. J. Poë, and K. Shaw, *J. Chem. Soc. (A)*, 1970, 1745.
[33] F. Monacelli and E. Viel, *Inorg. Chim. Acta*, 1967, **1**, 467; T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 1972, **94**, 8357.

$(NMeH_2)_5Cl]Cl_2$ (1.15 g) and zinc dust (1 g) in aqueous methylamine solution [5 cm³ of 40% (w/v) solution + 10 cm³ of water] to 323 K for *ca.* 5 min produced a vigorous reaction. Concentrated HCl was carefully added to the resulting pale yellow filtered solution at 273 K to give pH $\leqslant 6$. After adding KCl (1 g) and acidification to pH $\leqslant 1$, a *30% (w/v)* solution of hydrogen peroxide (2 cm³) was quickly added; the solution rapidly became orange-yellow and a yellow solid was precipitated. The mixture was diluted with 4 mol dm⁻³ HCl (50 cm³), transferred to a conical flask (250 cm³), and boiled vigorously for 30 min, with constant addition of 4 mol dm⁻³ HCl to keep the volume constant. On cooling, the clear orange solution gave orange-yellow lamellar crystals, which were filtered off, washed with cold 4 mol dm⁻³ HCl, and recrystallised from the minimum volume of 1 mol dm⁻³ HCl. The resulting product was washed with ethanol and dried *in vacuo.* Yield 0.78 g (74%).

R = Et, X = NO₃, *n* = 0. This complex was prepared as for the methylamine complex, using $[Rh(NEtH_2)_5Cl]$-$Cl_2 \cdot 0.5H_2O$ (0.36 g), zinc dust (1 g), and aqueous ethylamine [1 cm³ of 70% (w/v) solution + 4 cm³ of water]. After boiling, the hot solution was treated with concentrated HNO₃ (1 cm³). Yield 0.15 g (45%).

R = Prⁿ, X = Cl, *n* = 0. A mixture of $[Rh(NPr^nH_2)_5$-$Cl]Cl_2$ (1.40 g) and sodium chloride (8.0 g) was heated under reflux in aqueous ethanol (2 : 1, 75 cm³). After a few seconds the solution suddenly became bright orange and some rhodium metal appeared. At this point the reaction was quickly quenched by immersing the reaction flask in ice–water and adding concentrated HCl (2 cm³). The warm solution was filtered, evaporated to dryness, and the solid was extracted with methanol (5 × 10 cm³). The methanol extract was evaporated to dryness and the residue was dissolved in hot water (30 cm³). The hot orange solution was filtered and after addition of concentrated HCl (2 cm³) and cooling in ice the product was obtained as yellow crystals. Yield 0.52 g (42%).

R = Buⁿ, X = Cl, *n* = 0. This complex was prepared as for the propylamine analogue, using $[Rh(NBu^nH_2)_5Cl]Cl_2$ (0.35 g) and NaCl (7.0 g) in aqueous ethanol (3 : 2, 50 cm³). Yield 0.15 g (49%).

R = Buⁱ, X = Cl, *n* = 1. This complex was prepared as for the propylamine complex, using $[Rh(NBu^iH_2)_5Cl]$-$Cl_2 \cdot H_2O$ (0.20 g) and NaCl (5.0 g) in aqueous ethanol (1 : 1, 60 cm³). Yield 0.06 g (34%).

trans-*Dibromotetrakis(methylamine)rhodium*(iii) *bromide,* *trans*-$[Rh(NMeH_2)_4Br_2]Br$. A solution of *trans*-[Rh-(NMeH₂)₄Cl₂]Cl (0.42 g) in 2 mol dm⁻³ HBr (60 cm³) was heated under reflux for 7 h during which time the colour changed from orange-yellow to orange. Cooling in ice gave orange crystals which were refluxed with 2 mol dm⁻³ HBr (60 cm³) for another 3 h to ensure complete reaction. The crystals obtained on cooling were extracted with hot

water (*ca.* 50 cm³) in order to remove [Rh(NMeH₂)₃Br₃] and addition of 9 mol dm⁻³ HBr (15 cm³) to the clear orange filtrate followed by cooling in ice gave the product as orange crystals which were filtered off, washed with ethanol, and dried in air. Yield 0.45 g (77%).

Kinetic Measurements.—The formation of $[Rh(NRH_2)_5$-$Br]^{2+}$ (R = Me, Et, or Prⁿ) was monitored by measuring the increase in absorbance at 270 nm. The final absorbance, A_∞, was measured after at least $8t_{\frac{1}{2}}$ when the spectrum was in good agreement with that of the pure bromo-complex. For the reaction of *trans*-$[Rh(NRH_2)_4Cl_2]^+$ with bromide the increase in absorbance at 305 nm (R = Me or Prⁿ) or 290 nm (R = Et) was followed and A_∞ was obtained as above. When R = Me, the final spectrum was in good agreement with that of pure *trans*-$[Rh(NMeH_2)_4Br_2]^+$, whilst the final spectra when R = Et or Prⁿ were sufficiently similar to the latter to be able to conclude that the product was *trans*-$[Rh(NRH_2)_4Br_2]^+$ (R = Et or Prⁿ).

Linear first-order plots of $\log(A_\infty - A_t)$ against time were obtained for at least $3t_{\frac{1}{2}}$ and $2.75t_{\frac{1}{2}}$ for the pentakis- and tetrakis-(alkylamine) complexes respectively. In the case of the latter reactions, slow decomposition of the product appeared to occur at the highest temperatures employed, as shown by a slow but continuous change in A_∞ with time. However, the linearity of the rate plots for these temperatures was satisfactory.

Activation parameters were obtained by computer least-squares analysis of the dependence of $\log(k/T)$ on $1/T$. Values of the rate constant k obtained for $I = 0.2$ mol dm⁻³ were employed in each case.

Proton exchange. The pseudo-first-order rate constant for amino-proton exchange of *trans*-$[Rh(NMeH_2)_4Cl_2]Cl$ in D_2O at 295 K was determined by monitoring the intensity of the central peak of the methyl resonance at τ 7.58 in the 100 MHz n.m.r. spectrum; the intensity–time data were fitted to an exponential curve using the computer curve-fitting program PLOFIT obtained from the British Aluminium Co. The ' pH ' of the solution was measured at 295 K using a Radiometer PHM 4d pH meter in conjunction with a Radiometer G222C glass microelectrode and a Radiometer K4112 calomel reference microelectrode. The pH meter was calibrated using a standard phosphate buffer (pH 6.865 at 298 K). The pD was calculated using the empirical relation: [34] pD = ' pH ' + 0.4.

Polarography.—Solutions of the complexes ($[Rh^{III}] \simeq 10^{-4}$ mol dm⁻³) were made up in a supporting electrolyte of 0.1 mol dm⁻³ KCl (for chloro-complexes) or 0.1 mol dm⁻³ KBr (for bromo-complexes). Where necessary, aqueous ethanol (4 : 1) was used as solvent (see Table 3).

³⁴ P. K. Glasoe and F. A. Long, *J. Phys. Chem.,* 1960, **64,** 188.