The Mechanisms of the Reactions between Hydrido-complexes and Diazonium Salts. Part 2. The Reactions of *cis,mer*-[$RhHCl_2(PEtPh_2)_3$]

Richard A. Henderson
A.F.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ

The mechanisms of the reactions between *cis,mer*-[$RhHCl_2(PEtPh_2)_3$] and (p-$R'C_6H_4N_2$)BF_4 (R′ = Cl, Me, or MeO) have been investigated in both methanol and acetonitrile. The influence of acid, chloride, and the *para* substituent on the aryl group defines a mechanism common to both solvents. Upon dissolution of *cis,mer*-[$RhHCl_2(PEtPh_2)_3$], the solvento-species [$RhHCl_2(PEtPh_2)_2$(solvent)] is formed rapidly. Subsequent substitution of the solvent molecule for the diazonium cation gives the intermediate [$RhH(N_2C_6H_4R'$-$p)Cl_2(PEtPh_2)_2]^+$, in which the hydrido-group has been rendered sufficiently acidic that it is subsequently lost from the metal. Attack of chloride at the metal increases the basicity of the aryldiazenido-ligand sufficiently for it to be protonated and yield the aryldiazene product *trans,mer*-[$Rh(NHNC_6H_4R'$-$p)Cl_3(PEtPh_2)_2$]. The various influences of isotopic substitution of the hydrido-group in *cis,mer*-[$RhHCl_2(PEtPh_2)_3$] and in the acid have been explored for the reactions in acetonitrile.

In the previous paper[1] the mechanism of the 'insertion' reaction between *trans*-[$PtH(Cl)(PEt_3)_2$] and a variety of diazonium salts [equation (1)] was described. The 'activation' of the

$$trans\text{-}[PtH(Cl)(PEt_3)_2] + p\text{-}R'C_6H_4N_2^+ \longrightarrow trans\text{-}[Pt(NHNC_6H_4R'\text{-}p)Cl(PEt_3)_2]^+ \quad (1)$$

dinitrogen residue in this reaction involves proton dissociation from the metal, followed (after reorganisation of the co-ordination sphere) by recapture of the proton by the aryldiazenido-ligand to yield the aryldiazene product. The work described herein extends these previous studies to the analogous reactions of *cis,mer*-[$RhHCl_2(PEtPh_2)_3$] with diazonium salts in the presence of a chloride source, to yield the aryldiazene products [equation (2)]. The reaction has been studied both in

$$cis,mer\text{-}[RhHCl_2(PEtPh_2)_3] + p\text{-}R'C_6H_4N_2^+ + Cl^- \longrightarrow trans,mer\text{-}[Rh(NHNC_6H_4R'\text{-}p)Cl_3(PEtPh_2)_2] + PEtPh_2 \quad (2)$$

methanol and in acetonitrile. A similar mechanism is involved in the reactions of this co-ordinatively saturated complex to that found in the platinum system.

Results

Two stereoisomers of [$RhHCl_2(PEtPh_2)_3$] (**A**) (and of the analogous triphenylphosphine complex) have been isolated (the so-called α and β forms).[2] The kinetic studies have been performed exclusively with the α form, and the ^{31}P and ^{1}H n.m.r. spectra clearly demonstrate the *cis,mer* configuration of this isomer[3] (Table 1).

The reactions between *cis,mer*-[$RhHCl_2(PEtPh_2)_3$] and (p-$R'C_6H_4N_2$)BF_4 (R′ = NO_2, Cl, F, H, Me, or MeO) both in methanol and in acetonitrile were studied by stopped-flow spectrophotometry. Under all the conditions described herein the absorbance–time traces were exponential with an initial absorbance corresponding to that of (**A**), and a final absorbance corresponding to that of the derived aryldiazene product, *trans,mer*-[$Rh(NHNC_6H_4R'$-$p)Cl_3(PEtPh_2)_2$]. However when R = NO_2 the reaction is too rapid to be studied by the stopped-flow technique, and of the remaining diazonium salts, only when R = Cl, Me, or MeO are the absorbance changes sufficiently large to obtain accurate data. The products of these reactions, *trans,mer*-[$Rh(NHNC_6H_4R'$-$p)Cl_3(PEtPh_2)_2$] (R = Cl, Me, or MeO), have been isolated and fully characterised as shown in Table 1.

In general, the reactivity patterns observed in both methanol and acetonitrile are similar, and for this reason the results of both studies are described under common headings.

Kinetics in the Presence of HCl.—The reactions between complex (**A**) and (p-$ClC_6H_4N_2$)BF_4 in the presence of acid exhibit a first-order dependence upon the concentrations of both (**A**) and the diazonium salt. In addition, in acetonitrile there is an inverse dependence on the concentration of HCl [equation (3)], as shown in Figure 1(*a*). In methanol, there is a slightly more complicated rate equation (4) [see also Figure 1(*b*)].

$$k_{obs.} = (21.2 \pm 0.5)[p\text{-}ClC_6H_4N_2^+]/[HCl] \quad (3)$$

$$k_{obs.} = \frac{(1.67 \pm 0.11) \times 10^2[p\text{-}ClC_6H_4N_2^+]}{[p\text{-}ClC_6H_4N_2^+] + (0.11 \pm 0.01)[H^+]} \quad (4)$$

In equations (3) and (4), and throughout this paper, the acid concentration in acetonitrile is described in terms of HCl, but in methanol in terms of the proton, although for all studies the acid source is identical. It has been demonstrated earlier[4] that hydrogen chloride is a 'strong' acid in methanol, whereas in acetonitrile it is only poorly ionised (K_a = 1.26 × 10^{-9}),[5] rendering it a correspondingly weaker acid, as shown in equation (5). Thus at the relatively low concentrations of acid

$$HCl + CH_3CN \overset{K_a}{\rightleftharpoons} CH_3CNH^+ + Cl^- \quad (5)$$

employed in these studies, the predominant form of the acid in acetonitrile is HCl. Description of the concentration of acid in terms of HCl rather than CH_3CNH^+ is vindicated by studies of the reactions in the presence of (NEt_4)Cl (see below) which demonstrate that the small concentration of CH_3CNH^+ is not the 'active' form of the acid.

The kinetic data for the reactions with p-$ClC_6H_4N_2^+$ in the presence of acetonitrile and methanol are in Tables 2 and 3, respectively.

The kinetics of the reactions between complex (**A**) and p-$MeC_6H_4N_2^+$ or p-$MeOC_6H_4N_2^+$ both in methanol and in

Table 1. Analytical and spectroscopic characterisation of complexes

Complex	Analysis[a] (%) C	H	N	N.m.r. (δ/p.p.m.) $^1H^{b-d}$	$^{31}P^{c,e}$
$[RhHCl_2(PEtPh_2)_3]^f$	61.4 (61.6)	5.6 (5.6)	0.0 (0.0)	−15.3(1) [d of d of t, $J(P_AH)$ = 9.1, $J(P_BH)$ = 12.7, J(RhH) = 17.3, Rh–H]	−101.9(1) [d of t, J(PP) = 71.5, J(RhP) = 137.2, central P of *mer* phosphines], −114.7(2) [d of d, J(PP) = 71.2, J(RhP) = 96.6, extreme P of *mer* phosphines]
$[Rh^2HCl_2(PEtPh_2)_3]^g$	61.0 (61.6)	5.5 (5.6)	0.0 (0.0)		
$[Rh(NHNC_6H_4Cl\text{-}p)Cl_3(PEtPh_2)_2]$	57.2 (56.9)	5.1 (4.9)	3.6 (3.9)		−123.0 [d, J(RhP) = 83.5, *trans* phosphines]
$[Rh(NHNC_6H_4Me\text{-}p)Cl_3(PEtPh_2)_2]$	55.8 (55.6)	5.2 (4.8)	3.4 (3.7)	2.3(3) $[CH_3C_6H_4]$	−123.0 [d, J(RhP) = 83.8, *trans* phosphines]
$[Rh(NHNC_6H_4OMe\text{-}p)Cl_3(PEtPh_2)_2]$	54.3 (54.3)	4.8 (4.9)	3.5 (3.6)	3.8(3) $[CH_3OC_6H_4]$	−123.1 [d, J(RhP) = 83.8, *trans* phosphines]

[a] Calculated values are given in parentheses. [b] Values are relative to $SiMe_4$ as internal reference, recorded in C^2HCl_3. d = Doublet, t = triplet. [c] Relative intensities are given in parentheses, J values in Hz. [d] All complexes exhibit signals at *ca.* 1.0—2.0 (CH_3), *ca.* 3.0—3.5 (CH_2), and *ca.* 6.3—8.5 p.p.m. (C_6H_5 and $R'C_6H_4$). [e] Values are relative to $P(OMe)_3$ as external reference, recorded in CH_2Cl_2. [f] ν(RhH) 2 130m cm^{-1}. [g] $\nu(Rh^2H)$ 1 530m cm^{-1}.

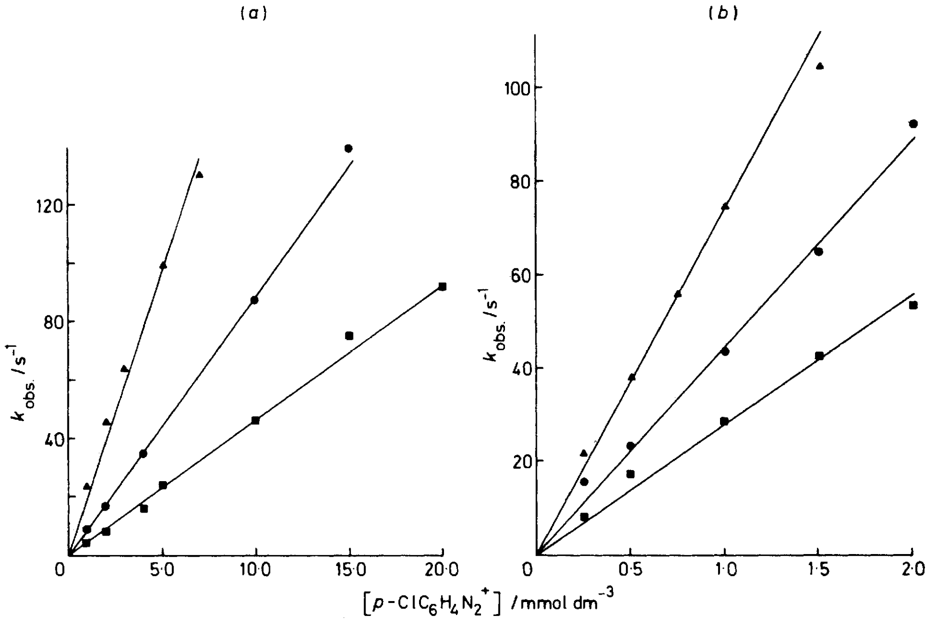


Figure 1. Dependence of the observed rate constant on the concentration of (p-$ClC_6H_4N_2$)BF_4 for the reaction with *cis,mer*-$[RhHCl_2(PEtPh_2)_3]$ ([Rh] = 1 × 10^{-4} mol dm^{-3}) in (*a*) acetonitrile and (*b*) methanol at 25.0 °C. Acid concentrations used: (*a*) [HCl] = 1 (▲), 2 (●), and 5 mmol dm^{-3} (■); lines drawn are those defined by equation (3); (*b*) [H$^+$] = 10.0 (▲), 20.0 (●), and 40.0 mmol dm^{-3} (■). Lines drawn are those defined by equation (4)

acetonitrile are very similar. In all cases the observed equation is of the form shown in (6), where [acid] represents HCl in

$$k_{obs.} = \frac{a[p\text{-}R'C_6H_4N_2{}^+]}{1 + b[p\text{-}R'C_6H_4N_2{}^+] + c[\text{acid}]} \qquad (6)$$

acetonitrile and H$^+$ in methanol, as discussed above. For R′ = Me; in acetonitrile, a = (8.3 ± 0.3) × 10^3, b = (2.9 ± 0.4) × 10^2, c = (1.5 ± 0.2) × 10^3; in methanol, a = (4.0 ± 0.1) × 10^4, b = (2.4 ± 0.2) × 10^2, c = (1.6 ± 0.1) × 10^2. For R′ = MeO: in acetonitrile, a = (5.3 ± 0.4) × 10^3, b = (2.1 ± 0.2) × 10^2, c = (2.4 ± 0.4) × 10^3; in methanol, a = (4.4 ± 0.4) × 10^4 dm^3 mol^{-1} s^{-1}, b = (2.7 ± 0.3) × 10^2 dm^3 mol^{-1}, c = 95.5 ± 0.5 dm^3 mol^{-1}. The kinetic data for the reactions of p-$MeC_6H_4N_2{}^+$ or p-$MeOC_6H_4N_2{}^+$ with (A) in acetonitrile and methanol are shown in Tables 2 and 3, respectively. The dependence of the observed rate constants on the concentrations of p-$MeC_6H_4N_2{}^+$ and HCl in acetonitrile is shown in Figure 2(*a*) and (*b*) respectively.

Kinetics in the Presence of HCl *and* (NEt_4)Cl.—The kinetics of the reaction between complex (A) and p-$MeC_6H_4N_2{}^+$ in the presence of acid in methanol is unaffected by the addition of (NEt_4)Cl (Table 4). However, the analogous reaction in acetonitrile is significantly accelerated by even low concentrations of (NEt_4)Cl as shown in Table 5. A complication that arises in interpreting these data is a consequence of the homoconjugation equilibrium (7). Using the literature value for K_H

Table 2. Kinetic data for the reactions of *cis,mer*-$[RhHCl_2(PEtPh_2)_3]$ with $(p\text{-}R'C_6H_4N_2)BF_4$ (R′ = Cl, Me, or MeO) and HCl in acetonitrile at 25.0 °C

R′	$[p\text{-}R'C_6H_4N_2^+]$	[HCl]	$k_{obs.}/s^{-1}$	
	mmol dm^{-3}			*
Cl	1.00	1.00	24.0	
	2.00		46.2	
	3.00		65.1	
	5.00		100.2	
	7.00		130.5	
	1.00	2.00	9.2	
	2.00		17.0	
	4.00		35.0	
	10.00		88.0	
	15.00		140.0	
	1.00	5.00	5.0	4.2
	2.00		8.0	8.0
	4.00		16.0	15.8
	5.00		24.2	25.0
	10.00		46.3	44.5
	15.00		76.1	75.9
	20.00		92.3	96.0
Cl	1.00	1.00	24.0	
		2.00	10.5	
		3.00	6.9	
		5.00	4.1	
		7.00	2.8	
		10.00	2.0	
	2.00	1.00	48.0	
		2.00	22.1	
		3.00	14.1	
		5.00	9.0	
		7.00	5.8	
		10.00	4.3	
Me	1.00	1.00	2.9	2.5
	2.00		5.4	4.4
	4.00		9.0	7.9
	6.00		11.9	10.4
	8.00		13.8	12.1
	10.00		15.4	13.5
	15.00		17.2	16.8
	20.00		21.6	18.8
	1.00	2.50	1.6	1.3
	2.00		3.2	2.4
	4.00		5.6	4.5
	6.00		7.5	6.4
	8.00		9.2	7.9
	10.00		10.8	8.5
	15.00		12.3	11.0
	20.00		15.9	13.9
	1.00	5.00	0.95	
	2.00		1.9	
	4.00		3.4	
	6.00		4.9	
	8.00		6.3	
	10.00		7.1	
	20.00		11.5	
Me	4.00	1.00	9.5	7.8
		2.00	6.9	5.1
		3.00	5.0	4.1
		4.00	4.3	3.9
		5.00	3.5	2.5
		7.00	2.2	2.0
		10.00	1.9	1.4
	6.00	1.00	12.2	10.5
		2.00	8.7	7.2
		3.00	6.7	5.6
		4.00	5.6	4.5
		5.00	5.2	3.7
		7.00	3.8	2.9
		10.00	2.3	2.2
MeO	1.00	1.00	1.5	2.1
	2.00		2.8	3.5
	4.00		5.2	6.6
	6.00		7.1	9.0
	8.00		8.0	11.1
	10.00		9.2	12.5
	15.00		12.7	15.2
	20.00		14.2	17.9
	1.00	2.50	0.7	1.1
	2.00		1.4	2.1
	4.00		2.5	4.0
	8.00		4.7	7.4
	10.00		5.9	8.3
	15.00		7.3	10.1
	20.00		9.1	13.2
	1.00	5.00	0.4	
	2.00		0.8	
	4.00		1.5	
	8.00		3.1	
	10.00		3.3	
	15.00		4.7	
	20.00		6.0	
	10.00	1.00	9.9	12.3
		2.00	6.7	9.1
		3.00	5.1	7.3
		4.00	4.0	6.2
		5.00	3.0	5.5
		7.00	2.5	4.3
		10.00	2.0	3.0
	20.00	1.00	14.0	17.7
		2.00	10.3	13.8
		3.00	8.8	12.0
		4.00	7.3	10.5
		5.00	5.7	9.3
		7.00	4.5	7.0
		10.00	3.5	5.9

* Studies using $[Rh^2HCl_2(PEtPh_2)_3]$ with ^2HCl.

$$HCl + Cl^- \overset{K_H}{\rightleftharpoons} HCl_2^- \qquad (7)$$

$(1.58 \times 10^2\ dm^3\ mol^{-1})$[5] to calculate the concentration of 'free' acid and chloride ion (designated by subscript f), the observed rate equation for the reaction between (**A**) and $p\text{-}MeC_6H_4N_2^+$ in the presence of HCl and $(NEt_4)Cl$ is as shown in (8). The dependence of the observed rate constants on the concentration of $p\text{-}MeC_6H_4N_2^+$ and $[HCl]_f/[Cl^-]_f$ is shown in Figure 3(*a*) and (*b*).

It is impossible to distinguish between HCl and CH_3CNH^+

Table 3. Kinetic data for the reactions of *cis,mer*-$[\text{RhHCl}_2(\text{PEtPh}_2)_3]$ with $(p\text{-R}'\text{C}_6\text{H}_4\text{N}_2)\text{BF}_4$ (R′ = Cl, Me, or MeO) and H^+ in methanol at 25.0 °C

	$[p\text{-R}'\text{C}_6\text{H}_4\text{N}_2^+]$	$[\text{H}^+]$	
R′	mmol dm^{-3}		$k_{\text{obs.}}$/s^{-1}
Cl	0.25	10.00	21.5
	0.50		38.0
	0.75		56.2
	1.00		75.0
	1.50		105.5
	0.25	20.00	16.5
	0.50		23.5
	1.00		44.0
	1.50		65.0
	2.00		93.2
	0.25	40.00	9.1
	0.50		17.5
	1.00		29.0
	1.50		42.8
	2.00		53.5
	0.25	1.00	100.0
		2.50	76.9
		5.00	45.5
		10.00	25.6
		20.00	15.5
		30.00	11.1
	0.50	1.00	125.0
		2.50	90.9
		5.00	66.7
		10.00	43.5
		20.00	22.7
		30.00	20.2
Me	0.25	2.00	7.1
	0.50		14.0
	1.00		25.5
	1.50		35.7
	2.00		44.4
	0.25	5.00	5.4
	0.50		10.4
	1.00		20.1
	2.00		35.0
	3.00		47.9
	4.00		58.0
	5.00		71.1
	8.00		86.1
	0.25	20.00	2.3
	0.50		4.6
	1.00		9.0
	2.00		17.1
	4.00		31.0
	6.00		42.7
	8.00		52.0
	0.25	1.00	8.0
		2.00	7.0
		4.00	6.0
		6.00	5.1
		10.00	3.7
		20.00	2.1
		30.00	1.5
Me	0.50	1.00	15.8
		2.00	13.5
		4.00	11.5
		6.00	9.8
		10.00	7.2
		20.00	4.8
		30.00	3.5
	1.00	1.00	27.5
		2.00	25.5
		4.00	21.0
		6.00	18.2
		10.00	14.1
		20.00	8.8
		30.00	6.5
MeO	0.50	2.50	15.5
	1.00		29.4
	2.00		48.9
	4.00		77.3
	0.50	5.00	13.8
	1.00		25.9
	2.00		44.0
	3.00		58.9
	4.00		69.0
	6.00		84.5
	0.50	20.00	7.0
	1.00		13.5
	2.00		26.1
	3.00		35.5
	4.00		44.0
	6.00		58.4
	8.00		69.0
	1.00	1.00	32.5
		2.00	30.5
		5.00	26.2
		10.00	19.8
		20.00	13.0
		30.00	10.8
	2.00	1.00	54.5
		2.00	50.5
		5.00	45.0
		10.00	35.8
		20.00	26.0
		30.00	20.8
	3.00	2.00	65.7
		3.00	63.3
		5.00	57.2
		10.00	49.1
		20.00	35.5
		30.00	29.5

$$k_{\text{obs.}} = \frac{(1.3 \pm 0.1) \times 10^{2}[p\text{-MeC}_6\text{H}_4\text{N}_2^+][\text{Cl}^-]_f}{[p\text{-MeC}_6\text{H}_4\text{N}_2^+][\text{Cl}^-]_f + (4.6 \pm 0.4) \times 10^{-3}[\text{Cl}^-]_f + (4.8 \pm 0.4) \times 10^{-3}[\text{HCl}]_f} \quad (8)$$

as the 'active' form of the acid in acetonitrile, on the basis of equation (6) alone. Rearrangement of equation (8) results in an equation of identical form to that of (6) except that the term $[HCl]_f/[Cl^-]_f$ replaces the [HCl] term. Clearly this ratio is proportional to $[CH_3CNH^+]$, and could indicate that such a term is present in equation (6). However, comparison of terms demonstrates that they are numerically very different. Certainly this demonstrates that in the presence of $(NEt_4)Cl$ a pathway different to that described by equation (6) is operative, and indicates that the 'active' form of the acid in this reaction is HCl. On this basis it is proposed (as shown earlier) that in the absence of $(NEt_4)Cl$ the acid is best described as HCl.

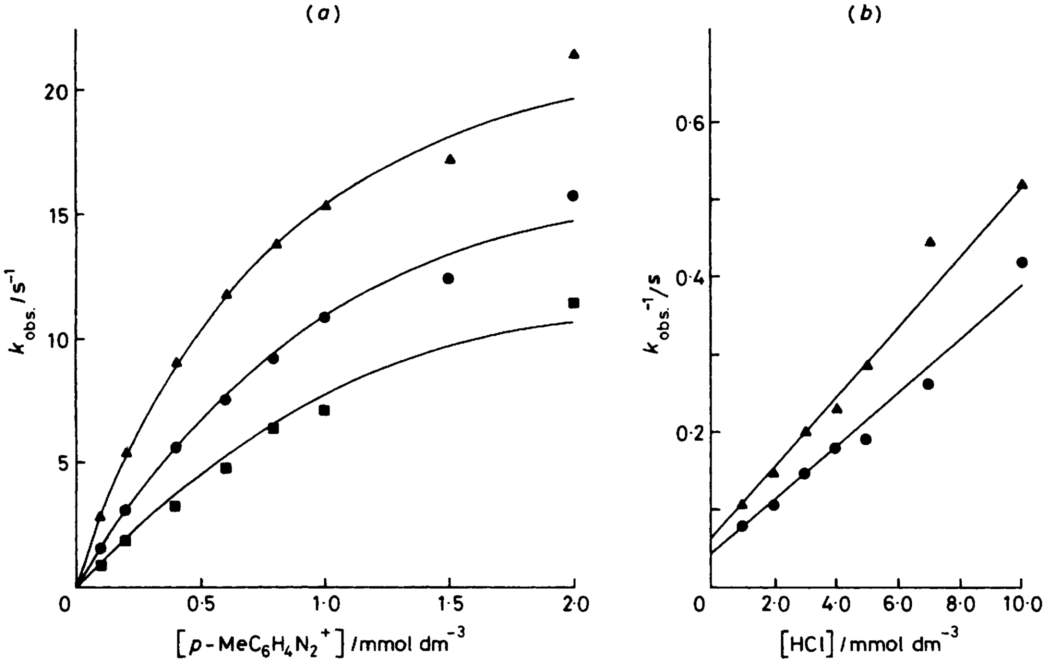


Figure 2. (*a*) Dependence of the observed rate constant on the concentration of (p-MeC$_6$H$_4$N$_2$)BF$_4$ for the reaction with *cis,mer*-[RhHCl$_2$(PEtPh$_2$)$_3$] ([Rh] = 1 × 10^{-4} mol dm^{-3}) in acetonitrile at 25.0 °C. Acid concentrations used: [HCl] = 1.0 (▲), 2.5 (●), and 5.0 mmol dm^{-3} (■). Curves drawn are those defined by equation (6). A similar behaviour is observed in the reactions with (p-MeOC$_6$H$_4$N$_2$)BF$_4$. (*b*) Dependence of $1/k_{obs.}$ on the concentration of acid for the reaction as in (*a*). Concentrations of diazonium salt used: [MeC$_6$H$_4$N$_2$$^+$] = 4.0 (▲) and 6.0 mmol dm^{-3} (■). Lines drawn are those defined by equation (6)

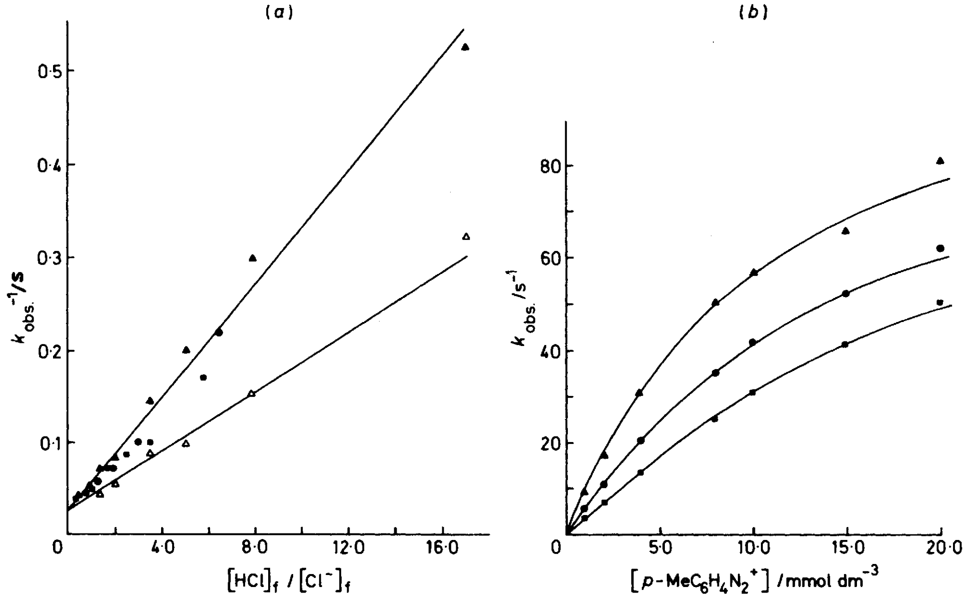


Figure 3. (*a*) Variation of $1/k_{obs.}$ with $[HCl]_f/[Cl^-]_f$ for the reaction of (p-MeC$_6$H$_4$N$_2$)BF$_4$ with *cis,mer*-[RhHCl$_2$(PEtPh$_2$)$_3$] ([Rh] = 1 × 10^{-4} mol dm^{-3}) in acetonitrile at 25.0 °C. Data for [MeC$_6$H$_4$N$_2$$^+$] = 2.0, [HCl] = 5.0 and [Cl$^-$] = 0—4.0 mmol dm^{-3} (△). Data for [MeC$_6$H$_4$N$_2$$^+$] = 1.0 mmol dm^{-3} with [HCl] = 2.5, [Cl$^-$] = 0—4.0 mmol dm^{-3} (●), [HCl] = 5.0, [Cl$^-$] = 0—4.0 mmol dm^{-3} (▲), and [HCl] = 1—7.0, [Cl$^-$] = 2.0 mmol dm^{-3} (■). Lines drawn are those defined by equation (8). (*b*) Dependence of the observed rate constants on the concentration of (p-MeC$_6$H$_4$N$_2$)BF$_4$ for the reaction as in (*a*) but with $[HCl]_f/[Cl^-]_f$ = 1.7 (▲), 3.5 (●), and 5.9 (■). Curves drawn are those defined by equation (8)

Table 4. Kinetic data for the reactions of *cis,mer*-$[RhHCl_2(PEtPh_2)_3]$ with $(p\text{-}R'C_6H_4N_2)BF_4$ (R′ = Cl, Me, or MeO) in the presence of LiCl [or $(NEt_4)Cl$] in methanol at 25.0 °C

R′	$[p\text{-}R'C_6H_4N_2^+]$	$[H^+]$	$[Cl^-]^a$	
	mmol dm⁻³			$k_{obs.}/s^{-1}$
Me	0.25	0.00	5.0	11.2
	0.50			21.3
	1.00			38.2
	1.50			55.0
	2.00			70.0
	0.50	0.00	5.00[b]	22.0
	1.00			38.5
	2.00			71.3
	0.25	0.00	20.00	10.8
	0.50			20.0
	1.00			36.3
	1.50			53.0
	2.00			68.4
MeO	0.25	0.00	5.00	8.5
	0.50			18.0
	1.00			31.3
	1.50			47.2
	2.00			64.0
	0.25	0.00	20.00	8.4
	0.50			17.8
	1.00			30.8
	1.50			47.8
	2.00			64.2
	1.00	1.00	1.00	70.0
			2.00	72.5
			5.00	74.4
			10.00	74.8
			20.00	74.1

[a] Chloride source is LiCl unless otherwise stated. [b] Chloride source is $(NEt_4)Cl$.

Kinetics in the Presence of $(NEt_4)Cl$.—The kinetics of the reactions between complex (**A**) and the diazonium salts in the absence of acid, but with an excess of chloride, is much simpler than observed so far in both solvents. Except for the reaction of $p\text{-}ClC_6H_4N_2^+$ with (**A**) in methanol (which is too rapid to be studied by the stopped-flow technique), all the reactions exhibit a first-order dependence on the concentration of diazonium salt, but are independent of the chloride-ion concentration or its source, as shown in equation (9). For R′ = Cl in acetonitrile:

$$k_{obs.} = d[p\text{-}R'C_6H_4N_2^+] \qquad (9)$$

$d = (3.0 \pm 0.2) \times 10^5$. For R′ = Me: in acetonitrile, $d = (2.7 \pm 0.2) \times 10^4$; in methanol, $d = (3.5 \pm 0.2) \times 10^4$. For R′ = MeO: in acetonitrile, $d = (2.6 \pm 0.2) \times 10^4$; in methanol, $d = (3.3 \pm 0.2) \times 10^4$ dm³ mol⁻¹ s⁻¹. These kinetic data for the reactions in methanol are shown in Table 4 and for the reactions in acetonitrile in Table 5.

Influence of Deuterium Substitution.—The effect of substituting deuterium for hydrogen [both in complex (**A**) and in the acid] in acetonitrile can be evaluated free from complications due to solvent exchange or solvent-isotope effects. The rate of the reactions between complex (**A**) and diazonium salts in the absence of acid is unaffected by isotopic substitution as shown in Table 5. For the reactions of (**A**) in the presence of acid, that with $p\text{-}ClC_6H_4N_2^+$ is unaffected by isotopic substitution [equation (3)] as shown by the data in Table 1. For the analogous reactions of $p\text{-}MeC_6H_4N_2^+$ and $p\text{-}MeOC_6H_4N_2^+$ the rate equation is of the form (6), but with marked numerical differences. When R′ = Me, $a = (8.3 \pm 0.3) \times 10^3$, $b = (2.9 \pm 0.2) \times 10^2$, $c = (2.1 \pm 0.2) \times 10^3$; when R′ = MeO, $a = (5.3 \pm 0.3) \times 10^3$ dm³ mol⁻¹ s⁻¹, $b = (1.8 \pm 0.2) \times 10^2$ dm³ mol⁻¹, and $c = (1.4 \pm 0.1) \times 10^3$ dm³ mol⁻¹. The kinetic data for these reactions are shown in Table 2.

Discussion

Qualitatively, the mechanistic pattern for the reactions of *cis,mer*-$[RhHCl_2(PEtPh_2)_3]$ (**A**) with $(p\text{-}R'C_6H_4N_2)BF_4$ (R′ = Cl, Me, or MeO) is very similar to that already found in the analogous reactions of *trans*-$[PtH(Cl)(PEt_3)_2]$.[1] The diazonium salts containing the more electron-withdrawing aryl substituents react fastest with (**A**), and the reactions are inhibited by acid. However, there are major differences between the two systems, particularly in the kinetics, which are attributable to the co-ordinatively-saturated nature of complex (**A**).

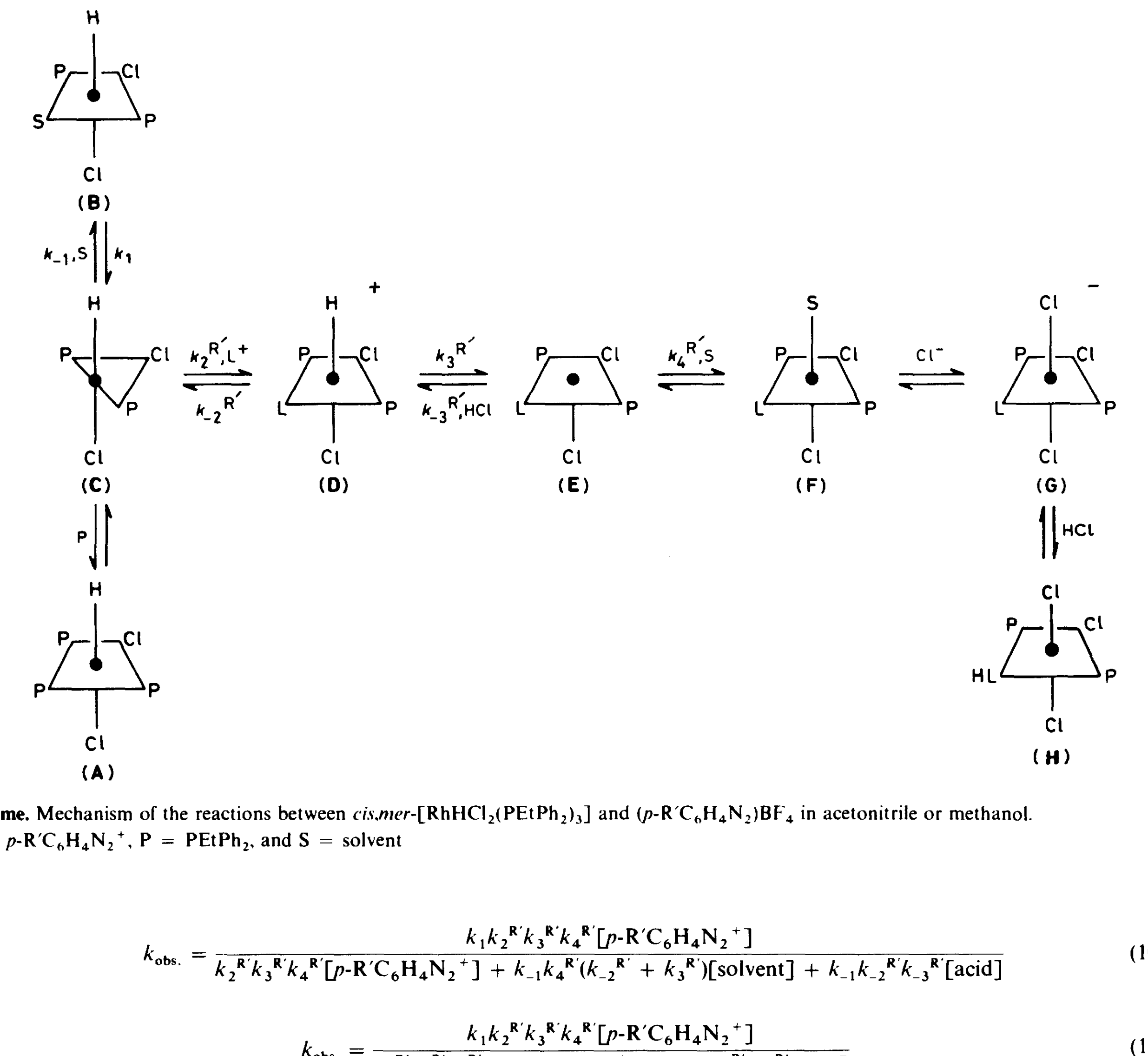
The complex $[RhHCl_2(PPh_3)_2]$ has been shown to 'insert' alkenes, alkynes,[6] and diazonium salts.[7] Early work formulated the products of the reactions with diazonium salts as solvated aryldiazenido-complexes,[8,9] but subsequently they have been reformulated as aryldiazene complexes, $[Rh(NHNC_6H_4R)Cl_3(PPh_3)_2]$.[7] The reactions of *cis,mer*-$[RhHCl_2(PEtPh_2)_3]$ with $(p\text{-}R'C_6H_4N_2)BF_4$ (R′ = Cl, Me, or MeO) in the presence of a chloride source yield *trans,mer*-$[Rh(NHNC_6H_4R'\text{-}p)Cl_3(PEtPh_2)_2]$ which have been isolated and characterised as shown in Table 1.

The kinetics of the reactions both in methanol and in acetonitrile can be rationalised by the mechanism shown in the Scheme. Upon dissolution, *cis,mer*-$[RhHCl_2(PEtPh_2)_3]$ (**A**) loses a phosphine which is replaced by a molecule of solvent to yield the species (**B**), presumably of the stereochemistry shown. Indeed it is the position of this substitution that defines the stereochemistry of the product (**H**). This lability of the central phosphine of the meridional set is almost certainly steric in origin. Similar lability has been proposed for $[RhCl(PPh_3)_3]$, and to account for the isolation of $[RhHCl_2(PPh_3)_2]$. The absence of an inverse dependence on the chloride-ion concentration in the kinetics [equations (8) and (9)] demonstrated that the loss of a phosphine *cis* to the hydrido-group is faster than chloride loss *trans* to the hydrido-group. This contrasts with the studies on *trans*-$[PtH(Cl)(PEt_3)_2]$,[1] but the *trans* effect in octahedral complexes is less marked.[10]

Subsequent substitution of the solvent molecule in (**B**) by the diazonium cation results in the intermediate (**D**), in which the electron density of the metal has been reduced, thus rendering the hydrido-group sufficiently acidic that it is lost as a proton yielding (**E**). Subsequent attack of solvent at the vacant site results in (**F**) and its relatively rapid substitution by the more electron-releasing chloro-group yields species (**G**) in which the aryldiazenido-ligand is rendered sufficiently basic to be protonated to yield the aryldiazene product (**H**).

It is important to note that from, and including, species (**F**) onwards the aryldiazenido-residue is forced to adopt the 'doubly bent' configuration (**I**), thus protonation of the species (**G**) results naturally in the aryldiazene product (**H**). The alternative 'singly bent' configuration of the aryldiazenido-ligand (**J**) would render (**F**) and (**G**), formally twenty-electron species, and yield arylhydrazido(2−)-complexes upon protonation.

The conclusion that intermediate (**D**) contains an aryldiazenido-ligand *cis* to the hydrido-group together with the co-ordinatively saturated nature of these species dictates that the present system is stereochemically very different to the platinum system,[1] where a strong *trans* effect dominates the substitution pattern.

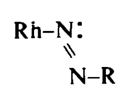


Scheme. Mechanism of the reactions between *cis,mer*-$[RhHCl_2(PEtPh_2)_3]$ and $(p\text{-}R'C_6H_4N_2)BF_4$ in acetonitrile or methanol. L = $p\text{-}R'C_6H_4N_2^+$, P = $PEtPh_2$, and S = solvent

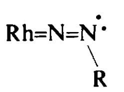
$$k_{\text{obs.}} = \frac{k_1k_2^{R'}k_3^{R'}k_4^{R'}[p\text{-}R'C_6H_4N_2^{\ +}]}{k_2^{R'}k_3^{R'}k_4^{R'}[p\text{-}R'C_6H_4N_2^{\ +}] + k_{-1}k_4^{R'}(k_{-2}^{R'} + k_3^{R'})[\text{solvent}] + k_{-1}k_{-2}^{R'}k_{-3}^{R'}[\text{acid}]} \tag{10}$$

$$k_{\text{obs.}} = \frac{k_1k_2^{R'}k_3^{R'}k_4^{R'}[p\text{-}R'C_6H_4N_2^{\ +}]}{k_2^{R'}k_3^{R'}k_4^{R'}[p\text{-}R'C_6H_4N_2^{\ +}] + k_{-1}k_{-2}^{R'}k_{-3}^{R'}[\text{acid}]} \tag{11}$$

Applying the steady-state hypothesis to the species (**C**)—(**E**), and assuming that capture of (**E**) by solvent is irreversible, the rate equation derivable from the Scheme is as shown in (10). An equation of identical form is obtained if dissociation of the solvent molecule from (**F**) is the slow step in the conversion into (**G**), and on the basis of the kinetics alone this possibility cannot be ruled out. However for the remainder of this discussion the simplified equation (10) will be employed. It is not possible to distinguish between steps k_1, k_2, k_3, or k_4 as the rate-limiting step purely on the basis of this rate equation.



(**I**)



(**J**)

The form of equation (10) is identical to that [equation (6)] found in the reactions of $p\text{-}MeC_6H_4N_2^{\ +}$ and $p\text{-}MeOC_6H_4N_2^{\ +}$ in methanol or acetonitrile. Comparison of equations (6) and (10) allows the evaluation of the elementary rate constants and some of the ratios as shown in Table 6.

The value of k_1 in a particular solvent is independent of the nature of the diazonium cation, but varies significantly with the solvent. This is consistent with the interpretation that the initial step of the reaction involves dissociation of a co-ordinated solvent molecule in (**B**), thus generating the co-ordinatively unsaturated intermediate (**C**). The complicated nature of the other functions do not lend themselves to ready interpretation of the relative magnitudes of the component elementary rate constants.

Depending upon the relative magnitudes of the denominator terms of equation (10), limiting forms of this general rate-equation can be observed. Thus if $k_2^{R'}k_3^{R'}k_4^{R'}[p\text{-}R'C_6H_4N_2^{\ +}] + k_{-1}k_{-2}^{R'}k_{-3}^{R'}[HCl] \gg k_{-1}k_{-4}^{R'}(k_{-2}^{R'} + k_3^{R'})[\text{solvent}]$, then equation (10) simplifies to (11). This is identical in form to the rate equation (4) for the reaction between complex (**A**) and $p\text{-}ClC_6H_4N_2^{\ +}$ in methanol. Comparison of the like terms in equation (4) and (11) again yields the corresponding values for the elementary rate constants, and a derived value of k_1 in excellent agreement with that found for the reactions with other diazonium salts (Table 6).

The final limiting form of equation (10) which is of relevance is that if $k_{-1}k_{-2}^{R'}k_{-2}^{R'}[HCl] \gg k_{-1}k_{-4}^{R'}(k_{-2}^{R'} + k_3^{R'})[\text{solvent}] + k_2^{R'}k_3^{R'}k_4^{R'}[p\text{-}R'C_6H_4N_2^{\ +}]$ then equation (10) simplifies to (12),

Table 5. Kinetic data for the reactions of *cis,mer*-[RhHCl$_2$(PEtPh$_2$)$_3$] with (p-R$'$C$_6$H$_4$N$_2$)BF$_4$ (R$'$ = Cl, Me, or MeO) in the presence of (NEt$_4$)Cl in acetonitrile at 25.0 °C

	[p-R$'$C$_6$H$_4$N$_2$$^+$]	[HCl]	[Cl$^-$]	
R$'$	mmol dm^{-3}			$k_{obs.}$/s^{-1}
Cl	0.10	0.00	5.00	42.0
	0.20			75.2
	0.40			125.0
	0.50			150.0
	0.70			200.0
	1.00			275.0
	0.50	0.00	1.00	150.5
			2.00	151.1
			5.00	150.0
			10.00	153.2
			20.00	154.6
Me	0.50	0.00	2.50	15.0
	1.00			29.5
	1.50			38.0
	2.00			54.2
	3.00			75.0
	0.50		5.00	15.0
				16.2[a]
	1.00			30.5
				29.0[a]
	1.50	0.00	5.00	39.5
				40.5[a]
	2.00			56.0
				53.2[e]
	3.00			80.0
				80.5[a]
	0.50	0.00	20.00	14.5
	1.00			29.5
	1.50			40.0
	2.00			52.2
	3.00			81.1
MeO	0.50	0.00	2.50	14.0
	1.00			27.0
	1.50			40.2
	2.00			52.0
	3.00			78.1
	0.50	0.00	5.00	15.2
	1.00			28.3
	1.50			37.8
	2.00			54.0
	3.00			78.0
	0.50	0.00	20.00	13.7
	1.00			26.7
	1.50			38.0
	2.00			52.3
	3.00			75.0
Me	1.00	2.50[b]	0.00[b]	1.6
			0.50	4.5
			1.00	9.5
			1.50	13.8
			2.00	17.1
			3.00	22.9
			4.00	24.2
		5.00[b]	0.00[b]	0.8
			0.50	2.0
			1.00	3.0
			1.50	5.0
			2.00	7.0
			3.00	12.3
			4.00	15.0
		1.00[b]	2.00[b]	0.44
		2.00		1.00
		3.00		1.69
		4.00		2.53
		5.00		3.50
		7.00		5.90
	2.00	5.00[b]	0.00[b]	1.1
			0.50	3.0
			1.00	6.3
			1.50	10.8
			2.00	11.8
			3.00	19.5
			4.00	23.5
	1.00	5.00[b,c]	2.00[b,c]	5.8
	2.00			11.2
	4.00			20.8
	8.00			35.1
	10.00			42.0
	15.00			52.0
	20.00			61.9
	1.00	3.00[b,d]	2.00[b,d]	9.4
	2.00			17.4
	4.00			31.3
	8.00			50.9
	10.00			57.0
	15.00			65.3
	20.00			80.5
	1.00	7.00[b,e]	2.00[b,e]	3.8
	2.00			7.2
	4.00			13.5
	8.00			25.2
	10.00			30.8
	15.00			41.5
	20.00			50.2

[a] Studies using [Rh^{2}HCl$_2$(PEtPh$_2$)$_3$]. [b] Values shown are not corrected for homoconjugation equilibrium [equation (7)]. [c] $[\mathrm{HCl}]_f/[\mathrm{Cl}^-]_f = 3.5$. [d] $[\mathrm{HCl}]_f/[\mathrm{Cl}^-]_f = 1.7$. [e] $[\mathrm{HCl}]_f/[\mathrm{Cl}^-]_f = 5.9$.

$$k_{obs.} = \frac{k_1 k_2^{R'} k_3^{R'} k_4^{R'}[p\text{-R}'\mathrm{C_6H_4N_2}^+]}{k_{-1} k_{-2}^{R'} k_{-3}^{R'}[\mathrm{HCl}]} \tag{12}$$

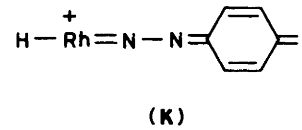
which is identical in form to that [equation (3)] for the reaction of complex (**A**) with p-ClC$_6$H$_4$N$_2$$^+$ in acetonitrile. Only by assuming the value of k_1 (derived from the studies with the other diazonium salts in acetonitrile) can any other quotient be obtained as shown in Table 6.

Thus the various rate equations for the reactions between complex (**A**) and (p-R$'$C$_6$H$_4$N$_2$)BF$_4$ in both methanol and acetonitrile, equations (3), (4), and (6), can be accommodated in terms of the derived generalised rate equation (10) and its limiting forms (11) and (12). Furthermore the inhibition of the reaction by acid as derived in equation (10) defines the pathway in which proton loss from the metal is an intimate feature, as indeed it is in the analogous reactions of *trans*-[PtH(Cl)-

Table 6. Summary of the rate parameters for the reactions between *cis,mer*-$[RhHCl_2(PEtPh_2)_3]$ and $(p\text{-}R'C_6H_4N_2)BF_4$ (R′ = Cl, Me, or MeO) in methanol and acetonitrile

R′	Solvent	k_1/s^{-1}	$\frac{k_2^{R'}k_3^{R'}}{k_{-1}(k_{-2}^{R'}+k_3^{R'})}$	$\frac{k_{-2}^{R'}k_{-3}^{R'}}{k_4^{R'}(k_{-2}^{R'}+k_3^{R'})}$	$\frac{k_2^{R'}k_3^{R'}k_4^{R'}}{k_{-1}k_{-2}^{R'}k_{-3}^{R'}}$	$\frac{k_2^{R'}}{k_{-1}}$	$\left(\frac{k_3^{R'}}{k_{-3}^{R'}}\right)^{H}\Big/\left(\frac{k_3^{R'}}{k_{-3}^{R'}}\right)^{D}$
Cl	MeOH	1.67×10^2			9.1		
Me		1.67×10^2	7.5×10^3	5.1×10^3	1.5		
			6.6×10^{3a}				
MeO		1.65×10^2	8.5×10^3	3.0×10^3	2.8		
			6.3×10^{3a}				
Cl	MeCN				0.75^b	5.6×10^{4a}	1.0
Me		28.4	7.1×10^3	3.7×10^4	0.19	5.1×10^{3a}	
		1.3×10^{2c}			2.1×10^{2c}	5.4×10^{3c}	
		28.6^d	7.1×10^{3d}	5.1×10^{4d}	0.14^d		1.3
MeO						4.6×10^{3a}	
		25.2	5.1×10^3	5.9×10^4	0.09		
		29.2^d	4.4×10^{3d}	2.4×10^{4d}	0.18		0.5

[a] Calculated from the studies in the absence of acid. [b] Calculated assuming $k_1 = 28.6\ s^{-1}$. [c] Calculated from the studies in the presence of HCl and $(NEt_4)Cl$. [d] Studies using $[Rh^2HCl_2(PEtPh_2)_3]$ and ^2HCl.



(K)

$(PEt_3)_2]$. The electronic influence of the *para*-aryl substituent on the diazonium cation has a similar effect on the rate of the reactions with complex (**A**) as it does with *trans*-$[PtH(Cl)(PEt_3)_2]$:[1] the more strongly electron withdrawing the substituent, the faster is the reaction. This is consistent with the mechanism shown in the Scheme since removal of electron density, by the *para* substituent, from the metal increases the acidity, and hence the lability, of the hydrido-group. As discussed before,[1] the relatively large distance between the *para*-substituent and the metal indicates contributions to the structure of (**D**) from the form (**K**). The relatively narrow range of *para* substituents employed in the present study, and the complicated nature of the derived rate parameters (Table 6), precludes a quantitative treatment of this effect.

In the absence of acid, but in the presence of $(NEt_4)Cl$ or LiCl, the reactions of the diazonium salts with complex (**A**) in both solvents exhibit the simple rate equation (9). At low acid concentration equation (10) simplifies to the form (13), which is equivalent to applying the steady-state treatment to species (**C**) and (**D**) from the Scheme. Equation (13) reduces to the observed form (9) if $k_{-1}(k_{-2}^{R'} + k_3^{R'})[\text{solvent}] \gg k_2^{R'}k_3^{R'}[p\text{-}R'C_6H_4N_2^+]$ as shown in equation (14).

$$k_{obs.} = \frac{k_1^{R'}k_2^{R'}k_3^{R'}[p\text{-}R'C_6H_4N_2^+]}{k_2^{R'}k_3^{R'}[p\text{-}R'C_6H_4N_2^+] + k_{-1}(k_{-2}^{R'} + k_3^{R'})[\text{solvent}]} \tag{13}$$

$$k_{obs.} = \frac{k_1k_2^{R'}k_3^{R'}[p\text{-}R'C_6H_4N_2^+]}{k_{-1}(k_{-2}^{R'} + k_3^{R'})[\text{solvent}]} \tag{14}$$

Clearly the values of the elementary rate constants will remain unchanged and this is a further check of the self-consistency of the mechanism proposed. Thus for the studies in methanol, comparison of equations (9) and (14) yields the values for $k_1k_2^{R'}k_3^{R'}/k_{-1}(k_{-2}^{R} + k_3^{R})$ of $(1.1 \pm 0.3) \times 10^6$ and $(1.0 \pm 0.3) \times 10^6\ s^{-1}$ for R′ = Me and MeO respectively. Using the values of k_1 obtained from the previous studies ($1.67 \times 10^2\ s^{-1}$, Table 6), values for $k_2^{R'}k_3^{R'}/k_{-1}(k_{-2}^{R'}+k_3^{R'})$ are 6.6×10^3 (R′ = Me) and 6.2×10^3 (R′ = MeO), in excellent agreement with values derived from the studies in the presence of acid (Table 6). Consistent with these interpretations, the kinetics of the reaction between complex (**A**) and $p\text{-}MeC_6H_4N_2^+$ in the presence of acid are unperturbed by the addition of $(NEt_4)Cl$.

In contrast an identical analysis of the reactions between (**A**) and $p\text{-}R'C_6H_4N_2^+$ (R′ = Me or MeO) in acetonitrile yields values of $k_2^{R'}k_3^{R'}/k_{-1}(k_{-2}^{R'} + k_3^{R'})$ markedly different (R′ = Me, 2.3×10^4; R′ = MeO, 2.2×10^4; R′ = Cl, 2.4×10^5) to the values obtained in the presence of acid (Table 6). The source of this discrepancy becomes clear when the influence of chloride on the reaction between complex (**A**) and $p\text{-}MeC_6H_4N_2^+$ in the presence of HCl is established.

The addition of $(NEt_4)Cl$ introduces, in effect, a good base into the system which can assist in the removal of the metal-bound proton (with a correspondingly changed rate constant for this step, k_5). Application of the steady-state hypothesis for the species (**C**)—(**E**), and allowing for this chloride-assisted deprotonation, the rate equation (15) can be derived. This reduces to the observed form (8) if $k_{-1}k_{-2}^{Me}k_{-4}^{Me}[\text{solvent}]$ is negligibly small compared to the rest of the denominator terms. Comparison of equations (8) and (15) allows the determination of some of the elementary rate constants: $k_1 = (1.3 \pm 0.1) \times 10^2\ s^{-1}$, $k_2^{Me}/k_{-1} = (5.4 \pm 0.4) \times 10^3$, $k_2^{Me}k_4^{Me}k_5^{Me}/k_{-1}k_{-2}^{Me}k_{-3}^{Me} = (2.1 \pm 0.4) \times 10^2\ dm^3\ mol^{-1}$, and hence $(k_4k_5/k_{-2}k_{-3})^{Me} = 0.04\ dm^3\ mol^{-1}$.

Consistent with this interpretation, the studies in the absence of acid in acetonitrile give rise to the limiting form of equation (15) shown in (16), which is equivalent to applying the steady-state treatment for species (**C**) and (**D**). Clearly to be consistent with the strict first-order dependence on the concentration of diazonium salt, and the independence of the chloride-ion concentration shown in equation (9), the $k_{-1}k_5^{Me}[Cl^-]$ term must dominate the denominator of equation (16) giving rise to (17). Comparison of equation (9) (R′ = Me) with (17) yields $k_1k_2^{Me}/k_{-1} = 6.6 \times 10^5\ s^{-1}$, and using the previously determined value of $k_1 = 1.3 \times 10^2\ s^{-1}$ derived from equation (15), yields $k_2^{Me}/k_{-1} = 5.1 \times 10^3$ in good agreement with the

$$k_{\text{obs.}} = \frac{k_1k_2^{\text{Me}}k_4^{\text{Me}}k_5^{\text{Me}}[p\text{-MeC}_6\text{H}_4\text{N}_2{}^+][\text{Cl}^-]_\text{f}}{k_2^{\text{Me}}k_4^{\text{Me}}k_5^{\text{Me}}[p\text{-MeC}_6\text{H}_4\text{N}_2{}^+][\text{Cl}^-]_\text{f} + k_{-1}k_{-2}k_4^{\text{Me}}[\text{solvent}] + k_{-1}k_4^{\text{Me}}k_5^{\text{Me}}[\text{Cl}^-]_\text{f}[\text{solvent}] + k_{-1}k_{-2}^{\text{Me}}k_{-3}^{\text{Me}}[\text{HCl}]_\text{f}} \quad (15)$$

$$k_{\text{obs.}} = \frac{k_1k_2^{\text{Me}}[p\text{-MeC}_6\text{H}_4\text{N}_2{}^+][\text{Cl}^-]}{k_2^{\text{Me}}k_5^{\text{Me}}[p\text{-McC}_6\text{H}_4\text{N}_2{}^+][\text{Cl}^-] + k_{-1}k_5^{\text{Me}}[\text{Cl}^-] + k_{-1}k_{-2}^{\text{Me}}} \quad (16)$$

$$k_{\text{obs.}} = k_1k_2^{\text{Me}}[p\text{-MeC}_6\text{H}_4\text{N}_2{}^+]/k_{-1}[\text{solvent}] \quad (17)$$

value derived from equation (15). Similar analysis, assuming the same value of k_1, yields $k_2^{\text{Me}}/k_{-1} = 4.6 \times 10^3$ and $k_2^{\text{Cl}}/k_{-1} = 5.4 \times 10^4$. Clearly the *para* substituent does have an influence on the rate of attack of the diazonium salt on the species (**C**), and from these, admittedly limited, data the diazonium cation in this reaction is best regarded as an electrophile rather than a poor nucleophile.

Although addition of $(\text{NEt}_4)\text{Cl}$ to the reaction between complex (**A**) and the diazonium salts in methanol has no effect, in acetonitrile the influence on the intimate mechanism is profound. Chloride is an effective base in the poorly basic aprotic solvent, and this provides a chloride-catalysed pathway for the deprotonation of (**D**). However this is not the only effect. At the very least, the presence of the chloride increases k_1 from 28.4 to 130 s^{-1}. It is unlikely that this can be acredited to the value of K_H [equation (7)][5] because of the internal consistency between equations (15) and (17), where the latter employs no assumption about the value of K_H. The difference can only be a consequence of specific outer-sphere interactions between (**B**) and $(\text{NEt}_4)\text{Cl}$ or to a rapid chloride-catalysed rearrangement of (**B**) to the isomer (**B′**) as shown in equation (18), where the

$$\underset{(\mathbf{B})}{cis\text{-}[\text{RhHCl}_2(\text{PEtPh}_2)_2(\text{CH}_3\text{CN})]} \longrightarrow \underset{(\mathbf{B'})}{trans\text{-}[\text{RhHCl}_2(\text{PEtPh}_2)_2(\text{CH}_3\text{CN})]} \quad (18)$$

stereochemical assignment refers to the disposition of the chloro-groups. The dissociation rate of acetonitrile *trans* to the hydrido-group is faster ($k_1 = 1.3 \times 10^2\ \text{s}^{-1}$) than that *cis* to the hydrido-group ($k_1 = 28.4\ \text{s}^{-1}$). Unfortunately, solubility problems preclude spectroscopic investigation of this isomerisation and in its absence the proposal must remain tentative. However it is consistent with the two forms known for $[\text{RhHCl}_2(\text{PEtPh}_2)_3]$,[2] and indeed iridium analogues,[3,11] in which a phosphine *trans* to the hydrido-group is labile to substitution by other phosphines.[12]

The influence of isotopic substitution of hydrogen for deuterium in both complex (**A**) and the acid on the rate of the reaction is a function of the diazonium salt employed. The reaction of $(p\text{-ClC}_6\text{H}_4\text{N}_2)\text{BF}_4$ with (**A**) in acetonitrile is unaffected by the isotopic substitutions, whereas the analogous reactions with $p\text{-MeC}_6\text{H}_4\text{N}_2{}^+$ and $p\text{-MeOC}_6\text{H}_4\text{N}_2{}^+$ are effected by these changes. Comparison of the corresponding numerical versions of equation (6) (with the deuterium labels) with equation (10) yields the parameters shown in Table 6.

The reactions of *cis,mer*-$[\text{Rh}^2\text{HCl}_2(\text{PEtPh}_2)_3]$ with the diazonium salts, in the absence of HCl, but in the presence of $(\text{NEt}_4)\text{Cl}$ exhibit no isotope effect, consistent with the rate equation (17). Assuming that only the values of $k_3^{\text{R}'}$ and $k_{-3}^{\text{R}'}$ are affected by isotopic substitution, the following ratios can be calculated: $(k_3^{\text{R}'})^\text{H}[k_{-2}^{\text{R}'} + (k_3^{\text{R}'})^\text{D}]/(k_3^{\text{R}'})^\text{D}[k_{-2}^{\text{R}'} + (k_3^{\text{R}'})^\text{H}] = 1.00 \pm 0.1$ ($\text{R}' = \text{Me}$), 1.20 ± 0.1 ($\text{R}' = \text{MeO}$); $(k_{-3}^{\text{R}'})^\text{H}[k_{-2}^{\text{R}'} + (k_3^{\text{R}'})^\text{D}]/(k_{-3}^{\text{R}})^\text{D}[k_{-2}^{\text{R}'} + (k_3^{\text{R}'})^\text{H}] = 0.75 \pm 0.1$ ($\text{R}' = \text{Me}$), 2.40 ± 0.1 ($\text{R}' = \text{MeO}$); and $(k_3^{\text{R}'}/k_{-3}^{\text{R}'})^\text{H}/(k_3^{\text{R}'}/k_{-3}^{\text{R}'})^\text{D} = 1.00 \pm 0.1$ ($\text{R}' = \text{Cl}$), 1.35 ± 0.1 ($\text{R}' = \text{Me}$), and 0.50 ± 0.1 ($\text{R}' = \text{MeO}$).

Little can be said with any conviction concerning these values because of the complicated nature of the ratios. However the different values for $(k_3^{\text{R}'}/k_{-3}^{\text{R}'})^\text{H}/(k_3^{\text{R}'}/k_{-3}^{\text{R}'})^\text{D}$ may be indicative of changes in the rate-limiting step, with the various aryl substituents.

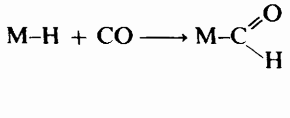
Conclusions

The single mechanism shown in the Scheme can accommodate the great variety of rate equations found under various conditions for the reactions of complex (**A**) with $(p\text{-R}'\text{C}_6\text{H}_4\text{N}_2)\text{BF}_4$ ($\text{R}' = \text{Cl}$, Me, or MeO). Furthermore, the mechanism of the reaction is essentially independent of the solvent (methanol or acetonitrile). The solvent's major roles are to act as a ligand for the rhodium atom [in species (**B**) and (**F**)] and to define the nature of the acid giving rise to the inhibition of the reaction. The intimate details of the mechanism are very similar to those established for the analogous reactions of *trans*-$[\text{PtH(Cl)(PEt}_3)_2]$,[1] in which proton loss from the metal, followed by reorganisation of the co-ordination sphere, allows proton recapture (but this time by the more basic aryldiazenido-ligand) to yield the aryldiazene product. A particularly interesting aspect of the present study, in which the *trans*-labilising effect of the hydrido-group does not dominate the reactivity, is that a group *cis* to the hydrido-ligand is the one replaced by the diazonium cation. Thus, although the *cis* disposition of these two groups is apparently advantageous for a migration reaction,[13] the lowest-energy pathway is still the deprotonation/reprotonation route outlined in the Scheme.

A major feature of the mechanism is the labilisation of the hydrido-group by the strongly electron-withdrawing diazonium cation in $[\text{RhH}(\text{N}_2\text{C}_6\text{H}_4\text{R}')\text{Cl}_2(\text{PEtPh}_2)_2]^+$ (**D**). Complexes containing both a hydrido- and an aryldiazenido-group are relatively rare and the complexes $[\text{MH(CO)(N}_2\text{Ph)(PPh}_3)_2]$ (M = Ru or Os) and $[\text{RuH(CO)}_2(\text{N}_2\text{Ph)(PPh}_3)_2]$ are the only examples,[14] where presumably the weaker acidity of the hydrido-group in these complexes precludes proton dissociation.

On the basis then of the mechanism established herein and in the preceding paper[1] it can be appreciated that in a more general sense the apparently analogous 'insertion' reactions of alkyl- and hydrido-complexes can adopt very different mechanisms. Particularly with strong electron-withdrawing substrates, the ability of the hydrido-group to be discharged as a proton can result in a low-energy pathway which is unavailable for the alkyl 'insertions.' This can have important ramifications. Whereas the migration of alkyl groups onto adjacent ligands is well established,[13] the factors influencing the 'insertion' mechanism described herein include (*i*) a strongly electron-withdrawing substrate and (*ii*) a flexible co-ordination sphere such that (*iii*) the substrate is rendered sufficiently basic to bind a proton.

This type of discussion may be particularly pertinent to the 'insertion' of carbon monoxide into metal–hydride bonds to form formyl complexes[15] as shown in equation (19). Although



$$\text{M–H} + \text{CO} \longrightarrow \text{M–C}\overset{\text{O}}{\underset{\text{H}}{}} \quad (19)$$

the mechanism of the 'insertion' of carbon monoxide into metal–alkyl bonds is well established,[16] the strong electron-withdrawing capability of the carbon monoxide ligand may dictate for hydrido-complexes a pathway analogous to that demonstrated herein. The evidence for an intramolecular migration process in these reactions is not compelling and the acidity of hydrido-carbonyl complexes is well documented.[17] Indeed the reaction of carbon monoxide with $[RhHCl_2(PPh_3)_2]$ results in the isolation of $[RhCl(CO)(PPh_3)_2]$.[6] If the intimate mechanism for the 'insertion' of carbon monoxide into metal–hydride bonds is similar to that described herein, the problem then becomes one of rendering the co-ordinated carbon monoxide sufficiently basic for it to be protonated.

Experimental

All manipulations in both the preparative and kinetic aspects of this work were performed under an atmosphere of dinitrogen using standard Schlenk-tube and syringe techniques. All solvents were dried and freshly distilled under dinitrogen immediately prior to use. The complexes *cis,mer*-$[Rh^xHCl_2(PEtPh_2)_3]$ (x = 1 or 2) were prepared by the literature methods;[2] *trans,mer*-$[Rh(NHNC_6H_4R'\text{-}p)Cl_3(PEtPh_2)_2]$ (R′ = Cl, Me, or MeO) were prepared by the method employed for the analogous triphenylphosphine complexes.[7]

trans,mer-*Trichloro(*p*-chlorophenyldiazene)bis(ethyldiphenylphosphine)rhodium.*—The complex $[RhHCl_2(PEtPh_2)_3]$ (0.3 g, 0.37 mmol) was dissolved in acetone (10 cm^3), $(p\text{-}ClC_6H_4N_2)BF_4$ (1.0 g, 4.42 mmol) was added, and the solution stirred for 0.5 h. Lithium chloride (1.0 g, 23.53 mmol) in ethanol (10 cm^3) was added to the dark red solution, and the volume reduced *in vacuo* until an orange solid precipitated. The product was removed by filtration, washed with ethanol and hexane, then dried *in vacuo*. It can be recrystallised from dichloromethane–ethanol.

The analogous *p*-methyl- and *p*-methoxy-phenyldiazene complexes were prepared in a similar manner. Analytical and spectroscopic characterisation of all the complexes is shown in Table 1.

The diazonium tetrafluoroborates $(p\text{-}R'C_6H_4N_2)BF_4$ (R′ = Cl, Me, or MeO) were prepared as described earlier.[1]

Kinetic Measurements.—All kinetic measurements were performed on an Aminco-Morrow stopped-flow spectrophotometer, and the preparation of all the samples was as described before.[1]

Acknowledgements

The enthusiastic assistance from Vicky Frost in all aspects of this work is gratefully acknowledged.

References

1 Part 1, V. L. Frost and R. A. Henderson, preceding paper.
2 A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc. A*, 1966, 1670.
3 J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7391.
4 R. A. Henderson, G. Davies, J. R. Dilworth, and R. N. F. Thorneley, *J. Chem. Soc., Dalton Trans.*, 1981, 40.
5 J. F. Coetzee, *Prog. Phys. Org. Chem.*, 1967, **4**, 45.
6 M. C. Baird, J. T. Mague, J. A. Osborne, and G. Wilkinson, *J. Chem. Soc. A*, 1967, 1347.
7 K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1973, 2713.
8 M. C. Baird and G. Wilkinson, *J. Chem. Soc. A*, 1967, 865.
9 G. W. Rayner-Canham and D. Sutton, *Can. J. Chem.*, 1971, **49**, 3994.
10 F. Basolo and R. G. Pearson, *Prog. Inorg. Chem.*, 1962, **4**, 381.
11 K. K. Chow, W. Levason, and C. A. McAuliffe, 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands,' ed. C. A. McAuliffe, Macmillan, London, 1973, p. 126.
12 J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1968, 617.
13 H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 7224.
14 B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 2784.
15 B. B. Wayland and B. A. Woods, *J. Chem. Soc., Chem. Commun.*, 1981, 700 and refs. therein.
16 T. C. Flood and K. D. Campbell, *J. Am. Chem. Soc.*, 1984, **106**, 2853 and refs. therein.
17 D. S. Moore and S. D. Robinson, *Chem Soc. Rev.*, 1984, **12**, 415.

Received 4*th January* 1985; *Paper* 5/037