The Displacement of the Heterocyclic Base R-py from $[Pd(dien)(R\text{-}py)]^{2+}$ (dien = 1,5-diamino-3-azapentane, R-py = 4-chloropyridine or 4-aminopyridine) by Water in Acid and Basic Solution and by Chloride. The Involvement of a Stable Five-co-ordinate Species

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The kinetics of displacement of R-py from the $[Pd(dien)(R\text{-}py)]^{2+}$ cation in acid and basic solution in the absence and presence of chloride ions are reported. In acid solution the rate of displacement of 4-chloropyridine is independent of $[H^+]$ but that for 4-aminopyridine is acid catalysed, the pyridylammonium ligand being a much better leaving group. In basic solution, the rate of displacement of 4-chloropyridine obeys the rate equation $10^3k_{obs.} = 8.7 + 11.5[OH^-] + 122[OH^-]^2\ s^{-1}$, while that for the 4-aminopyridine complex is independent of $[OH^-]$. The reaction between $[Pd(dien)(4Cl\text{-}py)]^{2+}$ and Cl^- leads to the rapid formation of a stable intermediate species which is in equilibrium with $[Pd(dien)Cl]^+$ and 4Cl-py. No such intermediate is observed in the reaction of the 4-aminopyridine complex which loses the ligand by the normal path for substitution in square-planar complexes. In the presence of acid the entry of Cl^- is irreversible and both substrates revert to the classical mechanism for ligand substitution.

The normal mode of ligand substitution at four-co-ordinate planar d^8 metal ions is associative in character and frequently involves passage through a five-co-ordinate intermediate. In general, such an intermediate is only transient and its presence is deduced from structure–activity relationships of many kinds.[1–3] Occasionally, the maximum concentration of the intermediate may be large enough for it to be detected by a substantial change in the kinetic form[4] and occasionally its inertness or stability may be sufficient for it to be detected in significant quantity[5] or even isolated and examined independently.[6] Recently we have observed that the system $[Pd(dien)(py)]^{2+} + [Pd(dien)Cl]^+ + py + Cl^-$ (py = pyridine, dien = 1,5-diamino-3-azapentane) contains the species $[Pd(dien)(py)Cl]^+$. When the total complex concentration is $>10^{-2}$ mol dm^{-3} this is the only significant palladium-containing species in a solution in which there is a large excess of Cl^- and a small excess of pyridine. We have reported the kinetics and equilibria of this system as well as those of other reactions of the $[Pd(dien)(py)]^{2+}$ cation[7] and, in order to understand the nature of this form of five-co-ordination and the factors that control it, we have prepared two other complexes of the type $[Pd(dien)(R\text{-}py)]^{2+}$, with R-py = 4-chloropyridine or 4-aminopyridine, so as to see how the properties of R-py, in particular its proton basicity, affect the electrophilicity and general reactivity of the palladium complex.

Experimental

Compounds and Reagents.—(*4-Chloropyridine*)(*1,5-diamino-3-azapentane*)*palladium*(II) *perchlorate*. Two molar equivalents of silver perchlorate were added, with the exclusion of light, to an ethanolic solution of [Pd(dien)Br]Br, prepared by the method of Baddley and Basolo,[8] and the solution was filtered from the precipitated AgBr. Slightly more than an equimolar amount of 4-chloropyridine was added and the solution was evaporated to small volume. On addition of a few drops of a concentrated solution of $LiClO_4$ in ethanol, pale yellow crystals separated and were filtered off and recrystallised from hot ethanol (Found: C, 20.60; H, 3.25; N, 10.90. $C_9H_{17}Cl_3N_4O_8Pd$ requires C, 20.85; H, 3.30; N, 10.75%).

(*4-Aminopyridine*)(*1,5-diamino-3-azapentane*)*palladium*(II)*perchlorate*. This was prepared in a similar way using a slight excess of 4-aminopyridine (Found: C, 21.40; H, 3.75; N, 14.10. $C_9H_{19}Cl_2N_5O_8Pd$ requires C, 21.50; H, 3.80; N, 13.95%).

All other reagents were either AR grade or else of the highest grade available.

Kinetics and Equilibria.—The reactions were initiated by mixing a freshly made solution of the complex in prethermostatted water with an equal volume of one containing all the other reagents previously brought to the reaction temperature. The subsequent reactions were followed spectrophotometrically using a Perkin-Elmer Lambda 5 spectrophotometer in the repetitive scanning mode (220—350 nm) if the reactions were slow enough or by following the absorbance at a selected wavelength as a function of time. The equilibrium measurements were made using the spectra determined when the reactions were complete. Ionic strength was kept constant using sodium perchlorate.

Proton n.m.r. spectra in D_2O were measured with a Varian FT 400 MHz spectrometer.

Results

(1) *Solvolytic Displacement of* R-py *from* $[Pd(dien)(R\text{-}py)]^{2+}$ *in Dilute Perchloric Acid and in Neutral Aqueous Solution.*—A dilute aqueous solution of $[Pd(dien)(4Cl\text{-}py)]^{2+}$ is stable indefinitely. The ^1H n.m.r. spectrum of a 10^{-2} mol dm^{-3} solution in D_2O shows two doublets at δ 8.572 ($H^{2,6}$ of py, 2 H) and 7.695 ($H^{3,5}$ of py, 2 H) with $^3J(H^2H^3) = {}^3J(H^5H^4) = 5.4$ Hz and an ABCX multiplet assigned to the dien protons consisting of a multiplet between δ 3.20 and 3.09 and a doublet at δ 2.83. The ^1H n.m.r. spectrum of a solution of $[Pd(dien)(4\ NH_2\text{-}py)][ClO_4]_2$ in D_2O (10^{-2} mol dm^{-3}) shows two doublets at δ 7.931 ($H^{2,6}$ of py, 2 H) and 6.691 ($H^{3,5}$ of py, 2 H) with $^3J(H^2H^3) = {}^3J(H^5H^4) = 5.8$ Hz and an ABCX multiplet associated with the dien protons consisting of a multiplet between δ 3.15 and 3.07 and a doublet at δ 2.83. The NH_2 protons exchange rapidly with the solvent and are not seen. However, this complex is not stable in dilute aqueous solution

Table 1. First-order rate constants for the displacement of 4-aminopyridine from $[Pd(dien)(4NH_2\text{-py})]^{2+}$ in acid aqueous solution at 25.0 °C.*

$10^3[H^+]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
1.0	1.50
5.0	1.57
10.0	1.62
30.0	1.68
50.0	1.80
100	1.98
300	3.00
500	4.20

* I = 1.00 mol dm^{-3} ($NaClO_4$). [Complex] = 1 × 10^{-4} mol dm^{-3}. Measurements made at 254 nm.

Table 2. First-order rate constants for the displacement of R-py from $[Pd(dien)(R\text{-py})]^{2+}$ in basic aqueous solution at 25.0 °C.*

$10^3[OH^-]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
R-py = 4-Chloropyridine	
5.0	8.71
10.0	8.77
20.0	9.00
30.0	9.20
50.0	9.50
83.3	10.4
90.9	10.8
R-py = 4-Aminopyridine	
5.0	0.168 ± 0.001
10.0	0.170 ± 0.001
20.0	0.162 ± 0.001
30.0	0.168 ± 0.001
50.0	0.165 ± 0.001

* I = 1.00 mol dm^{-3} ($NaClO_4$). [complex] = 1 × 10^{-4} mol dm^{-3}. Measurements made at 225 nm.

(10^{-4} mol dm^{-3}) and undergoes extensive solvolysis. While appearing to contradict the expectation that the greater the proton basicity of the ligand the more stable will its complex be, it appears that the basicity of the ligand is so great that the released amine deprotonates the aqua complex and the principal equilibrium that is observed in the absence of acid is as in equation (1).

$$[Pd(dien)(4NH_2\text{-py})]^{2+} + H_2O \rightleftharpoons [Pd(dien)(OH)]^+ + 4NH_2Hpy^+ \quad (1)$$

On adding dilute perchloric acid to a freshly prepared aqueous solution of $[Pd(dien)(R\text{-py})]^{2+}$ the spectra change in a way that is consistent with the displacement of the heterocyclic base R-py. When R-py = 4-chloropyridine the behaviour resembles that previously reported for the pyridine complex, the displacement of the amine being reversible. At the end of the change, which is not instantaneous, the equilibrium was measured spectrophotometrically, taking account of the protonation equilibrium of R-py.

$$[Pd(dien)(R\text{-py})]^{2+} + H_2O \overset{K_s}{\rightleftharpoons} [Pd(dien)(H_2O)]^{2+} + R\text{-py} \quad (2)$$

$$R\text{-py} + H^+ \overset{K_a}{\rightleftharpoons} R\text{-Hpy}^+ \quad (3)$$

$$[Pd(dien)(R\text{-py})]^{2+} + H_3O^+ \overset{K_{tot}}{\rightleftharpoons} [Pd(dien)(H_2O)]^{2+} + R\text{-Hpy}^+ \quad (4)$$

A series of spectra were measured at different $[H^+]$ and the most convenient wavelength (255 nm) chosen for the analysis. The best fit of the calculated curve to the experimental absorbance *versus* $[H^+]$ data over the range $0 < [H^+] < 0.010$ mol dm^{-3}, with $[complex]_{tot}$ = 2.50 × 10^{-4} mol dm^{-3}, I = 1.0 $NaClO_4$, using $\varepsilon_{(1)} = 2\,261 \pm 16$, $\varepsilon_{(2)} = 30 \pm 1$, $\varepsilon_{4Cl\text{-py}} = 2187 \pm 7$ and $\varepsilon_{4Cl\text{-Hpy}^+} = 5\,074 \pm 15$ cm^2 mmol^{-1} for the molar absorption coefficients of $[Pd(dien)(4Cl\text{-py})]^{2+}$, $[Pd(dien)(H_2O)]^{2+}$, 4Cl-py, and 4Cl-Hpy$^+$, respectively at 255 nm, is obtained when $K_{tot} = (3.3 \pm 0.1) \times 10^{-2}$. Since $K_{tot} = K_s/K_a$, inserting the literature value for K_a, 1.445 × 10^{-4} mol dm^{-3}, gives $K_s = (4.8 \pm 0.1) \times 10^{-6}$ mol dm^{-3}.

Complications arising from the protonation of the non-co-ordinating NH_2 group in 2-aminopyridine and the interference from the deprotonation of the co-ordinated aqua group dissuaded us from attempting to study the solvolytic equilibrium of its complex.

The kinetics of the approach to solvolytic equilibrium of acidified solutions of $[Pd(dien)(4Cl\text{-py})]^{2+}$ are consistent with those expected for the reversible first- and second-order processes indicated in reactions (2)—(4) (proton transfer is assumed to be very fast) and the solvolytic rate constant, k_s, was obtained by a non-linear regression of the absorbance *versus* time data to the calculated expression, with k_s as the parameter to be optimised. The standard expression [7] was derived from the relationships (5)—(7).

$$A = [(\mathbf{1})][\varepsilon_{(1)} - \varepsilon_{(2)} - \alpha_0\varepsilon_{4Cl\text{-py}} - (1 - \alpha_0)\varepsilon_{4Cl\text{-Hpy}^+}] \quad (5)$$

The ε values are as defined above and α_0, the fraction of released ligand that is unprotonated, is given by the expression $K_a/(K_a + [H^+])$.

$$[(\mathbf{1})] = \{c_0^2 + [(\mathbf{1})]_e\, c_0E\}/\{[(\mathbf{1})]_e + c_0E\} \quad (6)$$

where c_0 is the initial concentration of complex (2.54 × 10^{-4} mol dm^{-3}) and $[(\mathbf{1})]_e$ is the concentration of the 4-chloropyridine complex at equilibrium (calculated from the equilibrium constant determined in the previous section).

$$E = \exp(k_s t\{c_0 + [(\mathbf{1})]_e\}/\{c_0 - [(\mathbf{1})]_e\}) \quad (7)$$

For $[H^+]$ = 2.0 × 10^{-3} mol dm^{-3}, $k_s = (7 \pm 1) \times 10^{-3}$ s^{-1}. The solvolysis of the 4-aminopyridine complex is irreversible for $[H^+] \geqslant 10^{-3}$ mol dm^{-3} and the change in absorbance follows a first-order rate law. The derived rate constants, $K_{obs.}$, collected in Table 1, increase with increasing $[H^+]$ and obey the simple linear relationship $k_{obs.} = k_s + k_a[H^+]$.

(2) *Solvolytic Displacement of* R-py *from* $[Pd(dien)(R\text{-py})]^{2+}$ *in Basic Aqueous Solution.*—In the presence of base the spectra change to that of a solution containing equimolar amounts of $[Pd(dien)(OH)]^+$ and R-py. The kinetics are first order and the first-order rate constants $k_{obs.}$ are collected in Table 2. The rate constants for the displacement of 4Cl-py are dependent upon $[OH^-]$ and analysis of the data in Table 2 indicates a dependence of the type $k_{obs.} = k_s + k_{OH}[OH^-] + k_{OH'}[OH^-]^2$. The rate constants for the displacement of 4-aminopyridine are independent of $[OH^-]$ over the range $5 \times 10^{-3} \leqslant [OH^-] \leqslant 5 \times 10^{-2}$ mol dm^{-3}.

(3) *Reaction between* $[Pd(dien)(R\text{-py})]^{2+}$ *and Chloride in*

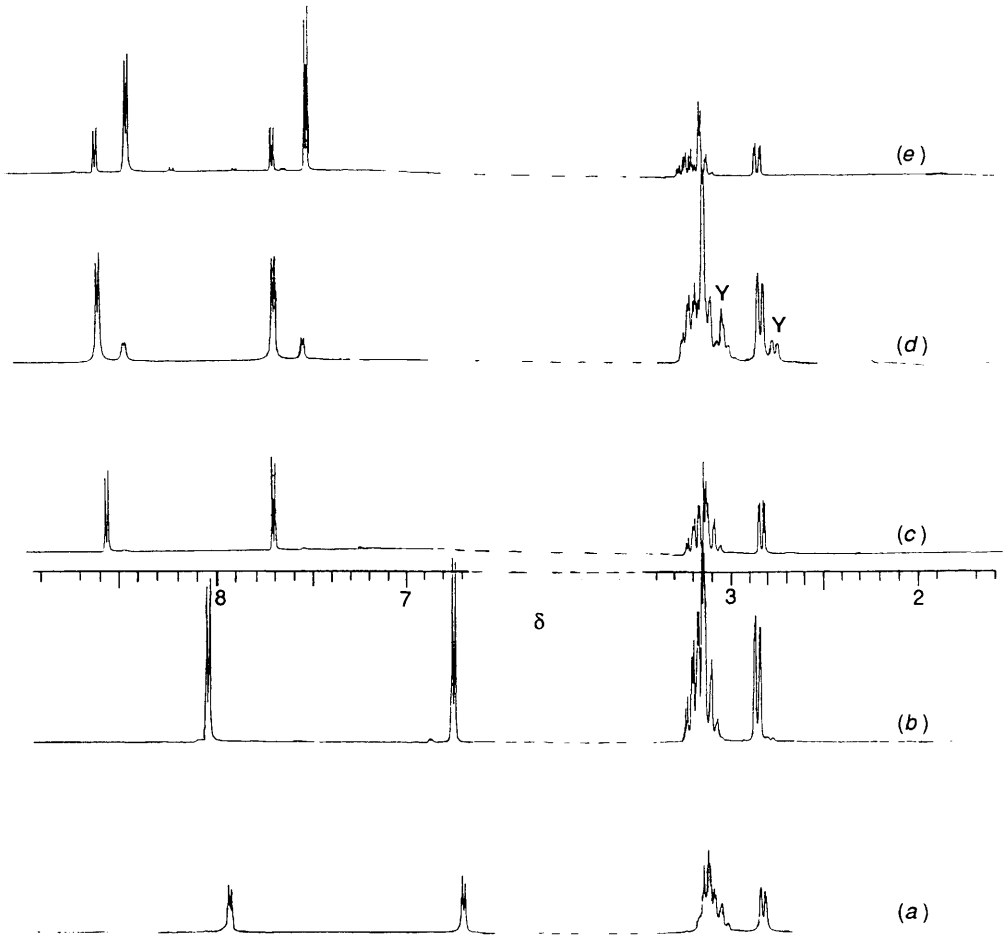

Figure. 400-MHz ^{1}H n.m.r. spectra of D_2O solutions of (*a*) $[Pd(dien)(4NH_2\text{-}py)][ClO_4]_2$ (10^{-2} mol dm^{-3}), (*b*) (*a*) + NaCl (5 mol dm^{-3}), (*c*) $[Pd(dien)(4Cl\text{-}py)][ClO_4]_2$ (10^{-2} mol dm^{-3}), (*d*) (*c*) + NaCl (5 mol dm^{-3}), and (*e*) (*d*) + 4Cl-py (3×10^{-2} mol dm^{-3}).

Aqueous Solution.—When excess of sodium chloride (*ca.* 5 mol dm^{-3}) is added to a solution of $[Pd(dien)(4Cl\text{-}py)][ClO_4]_2$ in D_2O the doublet at δ 8.572 is shifted to δ 8.619 while that at δ 7.695 is virtually unchanged at δ 7.702. Two new doublets appear at δ 8.479 and 7.547 and are assigned to the protons on free 4Cl-py. Addition of a three-fold molar excess of this species increases the height of the free-ligand peaks but does not cause any change in the chemical shift of the 4Cl-py protons on the co-ordinated ligand. The ABCX multiplet assigned to the dien methylene protons is likewise affected by the addition of chloride and a second doublet of doublets, assigned to the equivalent (Y) protons on $[Pd(dien)Cl]^+$, appears at 0.8 p.p.m. upfield. The addition of free 4-chloropyridine causes this latter signal to disappear but does not affect that of the 4-chloropyridine complex (Figure). The ^{1}H n.m.r. spectrum of $[Pd(dien)(4NH_2\text{-}py)]^{2+}$ in D_2O (10^{-2} mol dm^{-3}) is not affected by the addition of sodium chloride.

In dilute aqueous solution ([complex] = 1.6×10^{-4} mol dm^{-3}) the u.v. spectrum is affected by the addition of sodium chloride in a way that cannot be accounted for by the simple ligand-displacement equilibrium (8) but requires the formation

$$[Pd(dien)(4Cl\text{-}py)]^{2+} + Cl^- \overset{K}{\rightleftharpoons} [Pd(dien)Cl]^+ + 4Cl\text{-}py \quad (8)$$

of significant concentrations of an intermediate species that contains both chloride and 4-chloropyridine in the way indicated by the ^{1}H n.m.r. experiments reported above and observed previously in the reactions of the analogous pyridine complex. The absorbance *versus* [Cl^-] data are reported in Table 3. Analysis of the data in terms of the two equilibria (9) and (10) was made in terms of the relationships (11)—(13) using

$$\underset{(1)}{[Pd(dien)(4Cl\text{-}py)]^{2+}} + Cl^- \overset{K_{Cl}}{\rightleftharpoons} \underset{(2)}{[Pd(dien)(4Cl\text{-}py)Cl]^+} \quad (9)$$

$$\underset{(2)}{[Pd(dien)(4Cl\text{-}py)Cl]^+} \overset{K_1}{\rightleftharpoons} \underset{(3)}{[Pd(dien)Cl]^+} + 4Cl\text{-}py \quad (10)$$

$$\text{Absorbance} = \varepsilon_{(1)}[(1)] + \varepsilon_{(2)}[(2)] + \varepsilon_{(3)}[(3)] + \varepsilon_{4Cl\text{-}py}[4Cl\text{-}py] \quad (11)$$

$$K_{Cl} = [(2)]/[Cl^-][(1)] \quad (12)$$

$$K_1 = [(3)][4Cl\text{-}py]/[(2)] \quad (13)$$

the method of curve fitting described in ref. 7 with experimentally determined values for $\varepsilon_{(1)} = 14\,850$, $\varepsilon_{(3)} = 7920$, and $\varepsilon_{4Cl\text{-}py} = 2687$ cm^2 mmol^{-1} at 225 nm, and $\varepsilon_{(2)}$, K_{Cl}, and K_1 as parameters to be optimised. The agreement between the experimental points and the calculated values (also listed in Table 3) for $K_{Cl} = 3.41 \pm 0.28$ dm^3 mol^{-1} and $K_1 = (3.82 \pm 0.44) \times 10^{-5}$ mol dm^{-3} and $\varepsilon_{(2)} = 10\,200 \pm 200$ cm^2 mmol^{-1} is excellent; $\sigma = 0.0033$ of an absorbance unit.

Table 3. A comparison of the experimental values of A as a function of $[Cl^-]$ with those calculated for the equilibria (9) and (10) for the system [Pd(dien)(4Cl-py)] + Cl^- (see text).

$10^3[Cl^-]$/mol dm^{-3}	A	A_{calc}
0.00	1.700	1.699
1.00	1.640	1.640
2.00	1.612	1.615
3.00	1.599	1.596
4.00	1.577	1.580
5.00	1.565	1.566
10.0	1.507	1.510
20.0	1.435	1.433
30.0	1.382	1.376
40.0	1.326	1.330
50.0	1.292	1.291
100.0	1.155	1.155
200	1.004	1.009
300	0.933	0.929
400	0.876	0.877
500	0.841	0.840

Table 4. First-order rate constants for the reversible addition of Cl^- to $[Pd(dien)(R\text{-}py)]^{2+}$.*

$10^3[Cl^-]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
R-py = 4-Chloropyridine	
50	26.0
100	31.5
200	42.2
300	56.9
400	66.8
500	85.2
R-py = 4-Aminopyridine	
4	0.197
5	0.208
10	0.225
20	0.252
30	0.273
40	0.283
50	0.300
100	0.395
200	0.58
300	0.80
400	0.98
500	1.17

* In water at 25.0 °C, I = 1.00 mol dm^{-3} ($NaClO_4$).

As in the case of the pyridine complex, the approach to equilibrium on addition of chloride is not instantaneous and the first-order rate constants (Table 4) follow the rate equation $k_{obs.} = k_i + k_{Cl}[Cl^-]$, with $k_i = (1.8 \pm 0.2) \times 10^{-2}$ s^{-1} and $k_{Cl} = (1.28 \pm 0.06) \times 10^{-1}$ dm^3 mol^{-1} s^{-1}.

When NaCl (5 mol dm^{-3}) is added to a solution of $[Pd(dien)(4NH_2\text{-}py)]^{2+}$ in D_2O the peaks assigned to the pyridine protons shift but no significant signal is seen for the appearance of any free ligand. In dilute solution there is a significant change in spectrum. The final spectrum is independent of the amount of chloride added but the rate constant for the first-order process is linearly dependent on $[Cl^-]$, taking the form $k_{obs.} = k_s + k_2[Cl^-]$ (Table 5), with $k_s = (2.03 \pm 0.03) \times 10^{-4}$ s^{-1} and $k_2 = (1.97 \pm 0.05) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}.

(4) *Reaction between* $[Pd(dien)(R\text{-}py)][ClO_4]_2$ *and* Cl^- *in the Presence of Acid.*—Attempts to make a quantitative study of the effects of both acid and chloride on the kinetics of the displacement of pyridine from $[Pd(dien)(py)]^{2+}$ were unsuccessful because of contributions from the opening of one of the dien rings[7] but, in the presence of relatively small amounts of acid, this presents less of a problem with the 4-chloro- and 4-amino-pyridine complexes and serves to drive the reactions in which chloride becomes co-ordinated to palladium to completion by protonating the released heterocyclic base. The spectrum of the final product corresponded to that of $[Pd(dien)Cl]^+$ plus an equimolar amount of $R\text{-}Hpy^+$ and the spectral changes were first-order. The rate constants, collected in Table 5, follow the equation $k_{obs.} = k_s + k'_2[Cl^-]$, with $k_s = (7.9 \pm 0.1) \times 10^{-3}$ and $(1.5 \pm 0.1) \times 10^{-4}$ s^{-1}, and $k'_2 = (9.6 \pm 0.1) \times 10^{-2}$ and $(1.7 \pm 0.2) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, for the 4-chloro- and 4-amino-pyridine complexes respectively.

Discussion

The various derived rate constants are collected in Table 6 where they are compared with those previously published for the analogous pyridine complex.

In dilute acid solution the behaviour of the complexes is typical for square-planar d^8 metal-ion substrates, the solvolytic rate constant decreasing as the basicity of the leaving group is increased. The extra acid-dependent contribution to the rate of solvolysis of the 4-aminopyridine complex is readily explained in terms of the residual basicity of the free NH_2 group on this ambidentate ligand. There is little doubt that co-ordination to palladium is through the strongly basic heterocyclic nitrogen rather than through the NH_2 group whose basicity is likely to resemble that of aniline. The acid-dependent pathway can be represented by equations (14) and (15). The linearity of the

$$[Pd(dien)(NC_5H_4\text{–}NH_2)]^{2+} + H_3O^+ \overset{K_b}{\rightleftharpoons} [Pd(dien)(NC_5H_4\text{–}NH_3)]^{3+} + H_2O \quad (14)$$

$$[Pd(dien)(NC_5H_4\text{–}NH_3)]^{3+} + H_2O \xrightarrow{k'_s} [Pd(dien)(H_2O)]^{2+} + NC_5H_4NH_3^+ \quad (15)$$

dependence of $k_{obs.}$ on $[H^+]$ indicates that the data are all measured under conditions where $K_b[H^+] \ll 1$ and the slope, $k_a' = k_b k'_s = 5.3 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. Since the highest concentration of $[H^+]$ was 0.5 mol dm^{-3}, an upper limit is set for $K_b < 0.2$ dm^3 mol^{-1} and a lower limit for $k'_s > 2.5 \times 10^{-3}$ s^{-1} which is not inconsistent with the great reduction in the basicity of the heterocyclic nitrogen as a result of protonating the NH_2 group.†

The difference in the behaviour of the 4-chloropyridine and 4-aminopyridine complexes towards reactions with hydroxide throws more light upon the ever more common phenomenon of substitution reactions that have a mixed first- and second-order dependence on $[OH^-]$. A comparison of the data, together with that for the displacement of pyridine,[7] in Table 6 shows that the basicity of the leaving group plays a considerable part in determining the importance of this phenomenon. The relative contribution of the $[OH^-]^2$ term decreases strongly as the basicity of the leaving group is increased, and although the

† The pK_a of $4NH_3\text{-}Hpy^{2+}$ is likely to be similar to that of $4NO_2H\text{-}py^+$ (1.39[9]) in view of the fact that there is a linear relationship between the pK_a of 4-substituted pyridinium cations and the Hammett σ_p constant.[10] The group NMe_3^+ has a very similar substituent effect to NO_2 and NH_3^+ is not likely to be very much different.

Table 5. First-order rate constants for the displacement of R-py from $[Pd(dien)(R\text{-}py)]^{2+}$ by Cl^- in the presence of acid.[a]

$10^3[Cl^-]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
R-py = 4-Chloropyridine[b]	
4.9	8.5
10.8	9.2
22.3	10.3
33.8	11.0
39.3	11.4
50.5	12.7
198	27
227	30
R-py = 4-Aminopyridine[c]	
75	0.276
148	0.41
224	0.53
299	0.66
373	0.79

[a] In water at 25.0 °C, I = 1.00 mol dm^{-3} ($NaClO_4$). [b] $[H^+]$ = 5.17 × 10^{-2} mol dm^{-3}. [c] $[H^+]$ = 1.25 × 10^{-2} mol dm^{-3}.

Table 6. Summary of the derived rate constants for the various reactions of $[Pd(dien)(R\text{-}py)]^{2+}$.[a]

	R-py		
	4-Chloropyridine	Pyridine[b]	4-Aminopyridine
pK_a of R-Hpy$^+$	3.84	5.17	9.11
10^3k_s/s^{-1}	8.7	2.5	0.15
10^3k_{OH}/dm^3 mol^{-1} s^{-1}	11.5	6.3	*c*
$10^3k_{OH'}$/dm^6 mol^{-2} s^{-1}	122	8.1	*c*
10^6K_s/mol dm^{-3}	4.8	0.25	*d*
10^3k_i/s^{-1}	18	27.5[e]	*d*
10^3k_{-1}/s^{-1}	9	25	*d*
$10^5K_{Cl}K_1$	13	1.5	*d*
10^3k_2/dm^3 mol^{-1} s^{-1}	128	93	*d*
$10^3k'_2$/dm^3 mol^{-1} s^{-1}	96		1.7

[a] In aqueous solution at 25.0 °C, I = 1.00 mol dm^{-3}. [b] Data from ref. 7. [c] No dependence of rate on $[OH^-]$. [d] Could not be measured (see text). [e] Labelled k_a in ref. 7.

$[OH^-]$ term also decreases it does so to a much smaller extent. With a leaving group as basic as 4-aminopyridine, the $[OH^-]$ dependence is no longer detected. The same has been found in the analogous reactions of $[Pt(dien)(RCO_2)]^+$ when the basicity of the displaced carboxylate ligand is increased along the sequence R = CCl_3, $CHCl_2$, CH_2Cl[11] and perhaps it explains why there is no base catalysis of the displacement of NH_3 from $[Pd(NH_3)_4]^{2+}$.[12] One is drawn to the conclusion that the hydroxide dependence is, in part at least, due to a ground-state interaction between the substrate and OH^- that depends upon the electrophilicity of the central metal atom which diminishes as the basicity of the attached ligands is increased.

If sufficient acid is present to protonate the released pyridine (but not enough to cause opening of the dien rings or significant acid catalysis in the reactions of the 4-aminopyridine complex), the displacement of the pyridine by chloride obeys the classic substitution rate law for substitution in planar four-co-ordinate metal complexes, plots of k_{obs} *versus* $[Cl^-]$ being linear. The values of the intercepts are so close to those of the solvolytic rate constant, k_s, determined in the presence of a small excess of acid to justify representing the rate equation as $k_{obs} = k_s + k'_2[Cl^-]$. The rate constant for direct chloride substitution, k'_2, also reflects the basicity of the leaving group and the ratio of the rate constants for the two bases k'_2(4Cl-py)/k'_2(4NH_2-py) = 9.6 × 10^{-2}/1.7 × 10^{-3} = 56:1 is much the same as for the solvolytic reaction.

The reaction of these complexes with Cl^- in the absence of added acid still remains intriguing. The behaviour of $[Pd(dien)(4Cl\text{-}py)]^{2+}$ resembles that of the analogous pyridine species.[7] Both the ^1H n.m.r. and electronic spectra indicate that changes caused by adding excess of NaCl can only be accounted for by introducing significant quantities of a new species containing both chloride and base. Addition of a three-fold molar excess of free base will remove the small amount of $[Pd(dien)Cl]^+$ ion that is in equilibrium with the intermediate species but does not otherwise reverse the change. The spectral changes can be accounted for quantitatively in terms of two successive equilibria with constants K_{Cl} and K_1 [Reactions (9) and (10)] but the two values are closely correlated in the statistical analysis and any discussion based on the way in which these values depend upon the nature of the heterocyclic base is beyond the reliability of the data. The product, $K_{Cl}K_1$, which is equal to the equilibrium constant, K, for the process (8), is more precisely defined. This unusual behaviour is also reflected in the kinetics of the reaction with Cl^-. The rate equation for the approach to equilibrium takes the same form as that for the classical substitution process, *i.e.* $k_{obs} = k_i + k_2[Cl^-]$, but the value of k_i is more than twice that directly measured for the solvolytic process. The effect is far less marked than that observed for the corresponding pyridine complex, where k_i is some ten times greater than k_s, but it is still significant. As in the case of the pyridine complex, this rate equation is assigned to a reversible approach to equilibrium with k_{Cl} the forward rate constant and k_{-1} the reverse rate constant for equilibrium (9). The intercept of the plot of k_{obs} against $[Cl^-]$, k_i, is equal to the sum of k_{-1} and k_s since the solvolytic pathway offers an alternative route to the intermediate by way of two other processes that are very fast compared to those examined in this paper [equations (16) and (17)].

$$[Pd(dien)(H_2O)]^{2+} + Cl^- \xrightarrow{fast} [Pd(dien)Cl]^+ \quad (16)$$

$$[Pd(dien)Cl]^+ + \text{R-py} \xrightarrow{fast} [Pd(dien)(R\text{-}py)Cl]^+ \quad (17)$$

If the five-co-ordinate intermediate is traversed in the formation of the chloro square-planar product then the second-order rate constant associated with its formation, k_2, should be equal to that measured under irreversible conditions, k'_2. It has only been possible to measure both in the case of the 4-chloropyridine complex and the 30% difference observed is not totally outside experimental error.

The corresponding 4-aminopyridine complex does not show any anomalous behaviour. In the n.m.r. experiment, where [complex] = *ca.* 10^{-2} mol dm^{-3}, no significant amount of free base is observed at equilibrium, even in the presence of 5 mol dm^{-3} NaCl, which is to be expected in view of the much greater stability of the aminopyridine complex. However, there is no significant disturbance of the ^1H n.m.r. spectrum either. It must be concluded that the $[Pd(dien)(4NH_2\text{-}py)]^{2+}$ cation does not form significant amounts of an adduct with Cl^-.

The idea that the behaviour can be mapped out by choosing two substrates, one with a very basic R-py and the other with a weakly basic R-py, has proved to be unsatisfactory, and the formation of significant amounts of the chloride adduct seems to occur with a heterocyclic base of intermediate basicity. For the complex with the weakly basic 4-chloropyridine, the factor that promotes the binding of the chloride in the intermediate, *i.e.* the enhanced electrophilicity of the palladium resulting from the binding of a poor donor nitrogen base, also weakens the

intermediate with respect to subsequent loss of the amine. Although this is not reflected in the value of K_{Cl} derived from the analysis of the system at equilibrium, the kinetically derived value [$K_{Cl} = k_2/(k_i - k_s) = 11.6$ dm^3 mol^{-1}], is indeed considerably larger than that determined from the absorbance at equilibrium.

In the presence of both acid and chloride, the protonation of free R-py prevents the reverse part of reaction (10) and thereby completely destabilises the intermediate. The reaction reverts to the normal mode of substitution.

Acknowledgements

We thank the Italian Ministry of University and Research for financial support and we are grateful to Chris Cooksey for the measurement of the 400-MHz n.m.r. spectra and to Mrs. Lucia Gemelli for technical assistance.

References

1 C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1965.
2 L. Cattalini, *Prog. Inorg. Chem.*, 1970, **13**, 263.
3 M. L. Tobe, 'Comprehensive Coordination Chemistry,' vol. 1, eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, p. 311.
4 L. Cattalini, R. Ugo, and A. Orio, *J. Am. Chem. Soc.*, 1968, **90**, 4800.
5 G. Natile, L. Maresca, and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1977, 651.
6 L. Maresca, G. Natile, M. Calligaris, P. Delise, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1976, 2386.
7 L. Canovese, L. Cattalini, P. Uguagliati, and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1990, 867.
8 W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, 1969, **88**, 2949.
9 A. Fisher, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 1964, 3591.
10 C. D. Johnson, 'The Hammett Equation,' Cambridge University Press, London, 1973, p. 97.
11 L. Canovese, L. Cattalini, L. Gemelli, and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1988, 1049.
12 C. Blakeley, L. Cattalini, and M. L. Tobe, unpublished work.

Received 26*th March* 1990; *Paper* 0/01303J