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The Kinetics of Reactions of Some Chloro-aminepalladium(II) Complexes with Hydrochloric Acid.

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The kinetics of the reactions of hydrochloric acid with the complexes cis- *and* trans-$Pd(NH_3)_2Cl_2$, trans-$Pd(Et_2NH)_2Cl_2$, $PdenCl_2$, $PddienCl^+$, *and* $PdEt_4dienCl^+$ *have been followed spectrophotometrically.* The kinetic behaviour of the non-chelated complexes is quite conventional. The presence of hydrogen ions is necessary only to displace the equilibrium by neutralisation of the released ammonia or amine, and a two term rate law* $k_{obs}=k_1+k_2[Cl^-]$ *is observed. The behaviour of the chelated complexes is quite different, however, in that even the removal of the last coordinated nitrogen atom shows a dependence on hydrogen ion concentration and a complex dependence on chloride ion concentration is sometimes found. This behaviour is explicable in terms of a mechanism in which a five-coordinated reactive intermediate of the type* $[PdCl_4NH_2CH_2CH_2NH_3]^-$ *is stabilised by intramolecular hydrogen bonding, and only decomposes to form the product* $PdCl_4^{2-}$ *ion after attack by a further hydrogen ion. The complex dependence on chloride ion concentration suggests that this further attack by* H^+ *can be assisted in some way by the presence of an additional chloride ion. The activation parameters show that the kinetic* trans-*effects of ammonia and chloride are very similar, but that ammonia has a very much higher kinetic* cis-*effect than chloride.*

Introduction

Ligand interchange reactions of palladium(II) complexes are generally very rapid, and relatively few kinetic studies have been reported.[1] However, Pearson and Johnson[2] have recently studied some substitution reactions of acetylacetonatopalladium(II) complexes, and have found that replacement of the first *acac*$^-$ ligand from Pd $acac_2$ is measurably slow, and dependent on hydrogen ion concentration in a way characteristic of removal of chelated ligands.[3] We have made spectrophotometric studies of the kinetics of replacement of some chelating amine ligands by chloride ion in the presence of acid to see if similar behaviour occurs. Studies have also been made on some non-chelated ammine complexes.

(*) *en* = ethylenediamine; *dien* = diethylenetriamine; Et_4dien = 1,1,7,7,tetra-ethyldiethylenetriamine.
(1) C. H. Langford and H. B. Gray, «Ligand Substitution Processes», Benjamin, New York, Chap. 2 (1966).
(2) R. G. Pearson and D. A. Johnson, *J. Amer. Chem. Soc.*, *86*, 3983 (1964).
(3) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, *46*, 736 (1950); P. Krumholtz, *J. Phys. Chem.*, *60*, 87 (1956); A.K.S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959).

Experimental Section

Standard solutions of sodium chloride and sodium perchlorate were made up by weighing out the dry, finely powdered G.P.R. salts into graduated flasks, and dissolving them in distilled water. Standard lithium chloride solutions were prepared by dissolving the G.P.R. salt in distilled water, and analysing for chloride by Mohr's method. Technical grade diethylenetriamine and ethylenediamine were obtained from B.D.H. 1,1,7,7, tetra-ethyldiethylenetriamine was obtained from Ames Laboratories, Milford, Conn., U.S.A. G.P.R. diethylamine was obtained from Hopkins and Williams. Otherwise AnalaR grade reagents were used.

Chlorodiethylenetriaminepalladium(II) chloride was prepared by adding diethylenetriamine to palladium dichloride according to a published method,[4] but making use of concentrated lithium chloride solution instead of ammonium chloride. The complex was precipitated from solution by cooling in a refrigerator overnight, and was filtered off, washed with ice-cold water, dry ethanol and ether, and air-dried. (Yield: 25-30%).

Chloro-1,1,7,7,tetra-ethyldiethylenetriaminepalladium(II) chloride was prepared as follows. The triamine (2 ml.) was added to a solution of palladium dichloride (0.5 g.) in concentrated hydrochloric acid (1.3 ml.). Any solid that precipitated was redissolved by warming the solution on a steam bath. 6*M* aqueous lithium chloride solution (5 ml.) was then added, and the mixture cooled in a refrigerator. Bright yellow crystals were precipitated and these were filtered off, washed with ice-cold water and dry ethanol, and air-dried. This procedure gave rather low yields (~10%), and it as found to be preferable to prepare the corresponding bromo complex by using sodium bromide in place of lithium chloride. The initial product was recrystallised from a 50% ethanol-water mixture, and obtained as yellow needles. (Yield: 20%). The chloro complex was then made *in situ* as required, by

(4) F. Basolo, H. B. Gray and R. G. Pearson, *J. Amer. Chem. Soc.*, *82*, 4200 (1960).

dissolving a known weight of the bromo complex in 0.5*M* aqueous sodium chloride, and leaving the solution to stand for 24 hr. at room temperature. The ultraviolet and visible absorption spectra were then identical with those obtained from the isolated complex.

Dichloro-ethylenediaminepalladium(II) was prepared by the published method[5] and was obtained as yellow needles in 50% yield.

Trans-*dichlorodiamminepalladium(II)* was made in a way analogous to that for the ethylenediamine complex, but using AnalaR ammonia in place of the ethylenediamine. (Yield: 50%).

hydrochloric acid (5 ml.) at 70° for several hours, and the solution cooled and diluted to 100 ml. The final solution had a chloride concentration of 2.0*M* and an ionic strength of 4.5 *M*, maintained with sodium perchlorate. Under these conditions the molar extiction coefficient of the tetrachloropalladate(II) ion is $(11.2 \pm 0.05) \times 10^3$ l.mole^{-1} cm.$^{-1}$ at 279 mμ.[8] The weight of complex used was such as to given an optical density in 1 cm. or 1 mm. cells of about 0.4. This is the region of maximum sensitivity of the spectrophotometer which was a Unicam S.P. 500. The results are given in Table I, together with details of the main absorption maxima and their extinction coefficients.

Table I. Analytical data and some details of absorption spectra for some chloro-aminepalladium(II) complexes

	% Pd Found.	% Pd Calc.	λ (mμ)	ε (cm.$^{-1}$l.mole^{-1})
[a] *trans*-$Pd(NH_3)_2Cl_2$	50.9	50.3	380, 350, 250 (sh)	—, —, 3×10^3
[a] *cis*-$Pd(NH_3)_2Cl_2$	49.8	50.3	375, 290 (sh), 260 (sh)	—, 1.5×10^3, 4×10^3
[a] Pd enCl_2	44.8	44.8	373, 255 (sh)	—, —
[Pd dienCl]Cl	38.4	37.9	330	[b] 480
[Pd Et_4dienCl]Cl	25.5	27.1	350	[c] 900
[Pd Et_4dienBr]Br	22.1	22.1	362	[c] 740
trans-$Pd(Et_2NH)_2Cl_2$	33.3	32.9	No significant absorption above 300 mμ, absorbance rises steeply to a maximum below 230 mμ	

[a] The weaker absorption bands were detected in saturated solutions for which the concentrations were not known, and no extiction coefficients can be quoted. [b] cf. ε = 500, given by Baddley *et al.*, *Inorg. Chem.*, *2*, 921 (1963). [c] These values were obtained in a sufficient excess of free halide ion to suppress hydrolysis.

Cis-*dichlorodiamminepalladium(II)* was prepared by Grinberg's method.[6] Aqueous ammonium acetate (1.16 g. in 7.5 ml.) was added to aqueous sodium tetracholoropalladate(II) (0.5 g. in 5 ml.). After cooling for 40 min. in a refrigerator, the yellow solid formed was filtered off and washed with ice-cold water, and air-dried. (Yield: 60%). That this solid was different from the corresponding *trans* complex was demonstrated by reaction with iodide dissolved in acetone. The *trans* complex gave a pale yellow colour and the *cis* a dark red colour.[6] Doubt has recently been cast on the purity of the complex prepared in this way[7] but further discussion of this question will be postponed until later.

Trans-*dichlorobis(diethylamine)palladium(II)*. The amine (0.9 ml.) was added to a solution of sodium tetrachloropalladate(II) (0.5 g.) in 0.5*M* hydrochloric acid (10 ml.). The solution was filtered, slightly acidified with 2*M* hydrochloric acid and cooled in the refrigerator, and the yellow precipitate filtered off, washed with water, dry ethanol, and ether, and dried in air. (Yield: 45%). The assignment of the *trans* configuration was based on the preparative method used, and on the reaction with iodide in acetone solution.

The complexes were all analysed spectrophotometrically by conversion to tetrachloropalladate(II). A known weight of the complex was heated with 5*M*

(5) H. D. K. Drew, F. W. Pinkard, G. H. Preston and W. Wardlaw, *J. Chem. Soc.*, 1895 (1932).
(6) A. A. Grinberg and V. M. Shulman, *Compt. Rend. Acad. Sci. U.R.S.S.*, 215 (1933).
(7) R. Layton, D. W. Sink and J. R. Durig, *J. Inorg. Nuclear Chem.*, *28*, 1965 (1966); J. S. Coe and A. A. Malik, *Inorg. and Nuclear Chem. Letters*, *3*, 99 (1967).

The experimental values obtained are in good agreement with the theoretical ones, with the possible exception of the complex [PdEt_4dienCl]Cl. The value for this is low, probably because of the presence of some lithium chloride which was used to precipitate the rather soluble complex. The difference between the observed and calculated values are otherwise less than about 0.6%, almost half of which could be caused by the uncerrtainty in the extinction coefficient of the tetrachloropalladate(II) ion.[8] Any *trans*-$Pd(NH_3)_2Cl_2$ or $[Pd(NH_3)_4][PdCl_4]$ imprities in the *cis*-$Pd(NH_3)_2Cl_2$ would obviously not be detected by this analytical method, but the differences between the spectra of the supposedly *cis* complex and the *trans* complex are quite pronounced. The *trans* complex has two poorly resolved maxima at 350 and 380 mμ and the absorbance rises steeply to a shoulder at ~250 mμ, whereas the *cis* complex has one maximum at ~375 mμ, and the absorbance rises steeply to shoulders at 290 and 260 mμ. Any substantial *trans* impurity in the *cis* complex would be easy to detect.

Kinetic Studies. The reactions were studied by observing changes in absorbance in the ultraviolet region, as measured by a Unicam S.P. 500 or a Perkin Elmer 137UV spectrophotometer. The Perkin Elmer recording spectrophotometer was fitted with an Adkins, electrically controlled, thermostatted cell holder which holds cells of up to 1 cm. path-length, while the Unicam spectrophotometer was fitted with a Unicam cell holder which could hold cells of path-length up to 4 cm., and through which was circulated thermostatted liquids. The temperatures of the cells could thus be

(8) S. C. Srivastava and L. Newman, *Inorg. Chem.*, *5*, 1506 (1966).

controlled to better than ±0.1° over a temperature range from about 40 to 80°, in the Perkin Elmer spectrophotometer, and from about 5 to 90° in the Unicam spectrophotometer.

The majority of the runs were followed continuously in the thermostatted cells, but some of the slower ones were also followed by taking aliquots from a reaction mixture kept in a flask immersed in an oil bath at the required temperature. The aliquots were rapidly cooled, and their absorption spectra recorded. Ionic strengths were kept constant with perchlorate salts, and large excess of hydrogen and chloride ions were used so that the reactions were pseudo first order. Rate constants were determined graphically by plotting $\log(A_t - A_\infty)$ against t in the usual way. When beginning with the uncharged complexes, the reactions were followed in 5 or 10% aqueous ethanolic solution. The complexes were dissolved rapidly in 50% ethanol, and immediately diluted with suitable amounts of aqueous solutions of the other reagents.

Results

The trans-*$Pd(NH_3)_2Cl_2 \rightarrow PdCl_4^{2-}$ reaction.* The reaction of *trans*-$Pd(NH_3)_2Cl_2$ with hydrochloric acid in 5% aqueous ethanol was a two stage reaction, the second being characterised by isosbestic points at 246 and 257 mμ. Since the second stage turned out to be identical with the second stage of the reaction of *cis*-$Pd(NH_3)_2Cl_2$ under similar conditions, this is considered to be the reaction of the intermediate $Pd(NH_3)Cl_3^-$ ion, and the first stage corresponds to the reaction of *trans*-$Pd(NH_3)_2Cl_2$ to form $Pd(NH_3)Cl_3^-$. The reaction was studied at an ionic strength of 1.0*M* by following the growth in absorbance at 257 mμ, an isosbestic point for the second stage of the reaction. Absorbance changes from ~0.2 to ~0.6 in 4 cm. cells were obtained. The temperature was varied from 25 to 61°, the hydrogen ion concentration from 0.2 to 1.0*M*, and the chloride ion concentration from 0.1 to 1.0*M*. The rate plots were excellent, being linear for at least three half times of the reaction. The results are shown in Table II, and conform well to a two term rate law, (Figure 1), common to almost all reactions of planar d^8 complexes.[1]

Table II. Kinetic data for the reaction *trans*-$Pd(NH_3)_2Cl_2 \rightarrow Pd(NH_3)Cl_3^-$ in 5% aqueous ethanol (Followed at 257 mμ); $\mu = 1.0M$; $[\text{Complex}] \approx 5 \times 10^{-5}M$; $[H^+] = 1.0M$; absorbance changed from about 0.2 to 0.6 in 4 cm. cells

T (°C)	$[Cl^-]$ (M)	10^6k_{obs} (sec.$^{-1}$)	10^6k_1 [a] (sec.$^{-1}$)	10^6k_2 [a] (l.mole^{-1}sec.$^{-1}$)
25.0	0.75	8.8	3.7	6.9
25.0	1.00	10.6		
41.4	0.50	57.5		
41.4	0.80	73.6	27.6	59.8
41.4	1.00	87.5		
50.0	0.50	151		
50.0	0.70	183	73.0	154
50.0	1.00	211		
55.0	0.50	286	133	251
55.0	1.00	383		
60.8	0.10	220		
60.8	0.30	365		
60.8	0.50	488		
60.8	0.50	465 [b]	200	555
60.8	0.70	595		
60.8	1.00	723		

[a] Values calculated according to the rate law $k_{obs} = k_1 + k_2[Cl^-]$. [b] $[H^+] = 0.2M$.

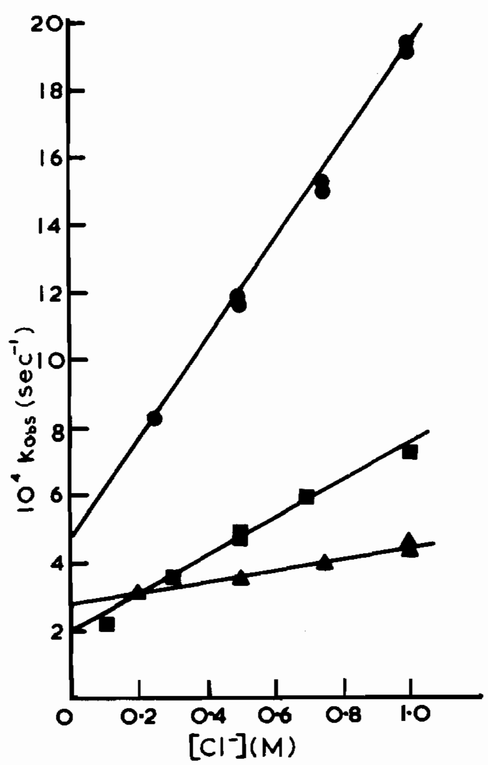


Figure 1. Plots of k_{obs} *versus* $[Cl^-]$. ●: *cis*-$Pd(NH_3)_2Cl_2$ at 25.0°; ■: *trans*-$Pd(NH_3)_2Cl_2$ at 60.8°; △: $Pd(NH_3)Cl_3^-$ at 65.3°.

The rates are independent of $[H^+]$ down to 0.2*M*. Activation enthalpies and entropies were derived graphically from the temperature dependence of the rate constants, excellent linear plots being obtained. These parameters are given in Table VI.

The cis-*$Pd(NH_3)_2Cl_2 \rightarrow PdCl_4^{2-}$ Reaction.* This reaction also occurs in two stages in 10% aqueous ethanol, the first stage exhibiting an isosbestic point at 330 mμ, and the second two, at 240 and 257 mμ. These isosbestic points for the second stage are almost identical with those for the second stage of the reaction of the *trans* complex. The first stage occurs readily at room temperature, whereas the second stage requires the temperature to be raised to about 75° before a similar rate is obtained. Reaction of the *cis* complex at room temperature with 0.5*M* perchloric acid leads to solutions which show an absorption maximum at 385 mμ. Subsequent addition of lithium chloride rapidly changes the spectrum to that of the product of the reaction with hydrochloric acid. This spectrum is similar to that described by Reinhardt *et al.*[9] for the complex $Pd(NH_3)Cl_3^-$, having an absorption maximum at ~430 mμ. No spectroscopic evidence for the presence of

(9) R. A. Reinhardt, N. L. Brenner and R. K. Sparkes, *Inorg. Chem.*, 6, 254 (1967).

the $PdCl_4^{2-}$ ion in the sample of the *cis* complex was obtained, and the clean kinetic behaviour described below precludes the presence of significant amounts of the $Pd(NH_3)_4^{2+}$ ion, which also reacts readily under these conditions. Although Layton *et al.*[7] obtained a variety of products from Grinberg's method of preparing the *cis* complex, the results seemed to be rather dependent on the exact conditions and we consider, on the our spectroscopic and kinetic evidence, that our samples of the *cis* complex were, perhaps fortuitously, quite pure. Samples were stored in a refrigerator for not more than 3 days before use in order to prevent isomerisation.[7] Even after 3 months the samples still showed the characteristic reaction with iodide, so a substantial proportion of *cis* complex must still have been present after that time. We therefore conclude that the first stage is the conversion of the *cis*-$Pd(NH_3)_2Cl_2$ into $Pd(NH_3)Cl_3^-$.

Table III. Kinetic data for the reaction *cis*-$Pd(NH_3)_2Cl_2 \rightarrow Pd(NH_3)Cl_3^-$ in 10% aqueous ethanol (Followed at 257 mμ); [Complex] $\sim 1.6 \times 10^{-4}M$; absorbance changed from 0.2 to 0.5 in 1 cm. cells

(i) $\mu = 1.0M$, $[H^+] = 1.0M$

T (°C)	$[Cl^-]$ (M)	10^4k_{obs} ($sec.^{-1}$)	10^4k_1 ($sec.^{-1}$)	10^4k_2 ($l.mole^{-1}sec.^{-1}$)
5.0	0.50	1.23		
5.0	0.75	1.58	0.518	1.40
5.0	1.00	1.89		
14.8	0.50	3.90		
14.8	0.75	5.06	1.61	4.83
14.8	1.00	6.53		
25.0	0.25	8.36		
25.0	0.50	11.8		
25.0	0.50	11.9 [a]		
25.0	0.75	15.3		
25.0	0.75	15.0 [a]	4.8	14.0
25.0	1.00	19.4		
25.0	1.00	19.2 [a]		
25.0	1.00	19.8 [b]		
25.0	1.00	19.6 [c]		

(ii) $\mu = 5.0M$, $[H^+] = 5.0M$

T (°C)	$[Cl^-]$ (M)	10^4k_{obs} ($sec.^{-1}$)	10^4k_2 ($l.mole^{-1}sec.^{-1}$)
5.0	1.00	1.15	
5.0	2.50	3.00	1.18
5.0	5.00	5.95	
14.8	2.00	7.11	
14.8	3.00	10.8	3.41
14.8	4.00	13.7	
25.0	1.00	11.5	
25.0	1.00	11.8 [d]	
25.0	1.50	16.6	10.7
25.0	2.0	22.2	
25.0	2.5	24.2	

[a] In 5% aqueous ethanol. [b] $[H^+] = 0.50M$. [c] $[H^+] = 0.20M$. [d] $[H^+] = 1.0M$.

The kinetics were followed by observing the growth of the absorbance at the isosbestic point of the second stage at 257 mμ. Absorbance changes from ~ 0.2 to ~ 0.5 were obtained in 1 cm. cells. Ionic strengths of 1.0 and 5.0*M* were used, and the dependence of the rates on the concentrations of hydrogen and chloride ions, and on the temperature, were studied. The results are shown in Table III. The observed rate constants again follow the two term rate law (Figure 1) and are independent of hydrogen ion concentration above $[H^+] = 0.2M$. At $\mu = 5.0M$, the term k_1 is too small for an accurate activation energy to be obtainable, but the activation parameters for the first order term at $\mu = 1.0M$, and for the second order terms at $\mu = 1.0$ and 5.0*M*, were determined graphically and are given in Table VI. Some reactions were also followed at $\mu = 1.0M$ in 5% aqueous ethanolic solution, and no dependence of the rates on the ethanol concentration was detected.

The $Pd(NH_3)Cl_3^- \rightarrow PdCl_4^{2-}$ Reaction. This reaction in 5% aqueous ethanolic solution was followed by studying the increase in absorbance at 279 mμ during the second stages of the reactions of *cis*- and *trans*-$Pd(NH_3)_2Cl_2$. Absorbance changes from ~ 0.1 to 0.7 were found in 1 cm. cells. When the starting complex was the *trans* isomer, excellent rate plots were obtained after 3 to 4 reaction half times of the *trans* complex had elapsed. The rate plots obtained by beginning with the *cis* complex were linear, and agreed with those beginning with the *trans* complex, only over the last 20% of the reaction, although the isosbestic points remained clear over most of the reaection. Because of the better rate plots obtained by beginning with the *trans* complex most of the studies made use of this complex. The results are summarised in Table IV.

Table IV. Kinetic data for the reaction $Pd(NH_3)Cl_3^- \rightarrow PdCl_4^{2-}$ (second stage of reaction of *trans*-$Pd(NH_3)_2Cl_2$ with HCl in 5% aqueous ethanol; followed at 279 mμ; [Complex] = 6 to 8, $\times 10^{-5}M$; absorbance changed from 0.1 to 0.7 in 1 cm. cells)

(i) $\mu = 1.0M$; T = 65.3°

$[H^+]$ (*M*)	$[Cl^-]$ (*M*)	10^4k_{obs} ($sec.^{-1}$)
1.0	0.20	3.16
1.0	0.50	3.53
1.0	0.75	3.59
1.0	1.0	4.49
0.1	1.0	4.53
0.01	1.0	4.57
0.004	1.0	4.29

$10^4k_1 = 2.8$ $sec.^{-1}$; $10^4k_2 = 1.7$ $l.mole^{-1}$ $sec.^{-1}$.

(ii) $\mu = 5.0M$; T = 50.0°

$[H^+]$ (*M*)	$[Cl^-]$ (*M*)	10^5k_{obs} ($sec.^{-1}$)	10^5k_2 ($l.mole^{-1}sec.^{-1}$)
1.0	5.0	23.8	4.76
1.0	5.0	24.6 [a]	4.92 [a]
3.0	5.0	23.6	4.72
3.0	5.0	24.0 [a]	4.80 [a]
5.0	5.0	23.2	4.64
5.0	5.0	23.8 [a]	4.76 [a]
5.0	3.0	13.2	4.40
5.0	1.0	4.23	4.23

(iii) $\mu = 5.0M$; $[H^+] = 5.0M$; $[Cl^-] = 1.0M$

T (°C)	40.0	50.0	54.8	60.2	64.8
10^5k_{obs} ($sec.^{-1}$)	1.31	4.23	7.38	12.6	20.9

[a] Second stage of reaction of *cis*-$Pd(NH_3)_2Cl_2$ with HCl.

At $\mu=1.0M$, a two term rate law is obeyed and the rates are independent of $[H^+]$ down to a concentration of $4\times10^{-3}M$. At $\mu=5.0M$, the rates are independent of $[H^+]$ above the lowest value used of $1.0M$ and are first order in $[Cl^-]$, the k_1 term being negligible. The activation parameters were determined graphically and are given in Table VI.

The trans-$Pd(Et_2NH)_2Cl_2\rightarrow PdCl_4^{2-}$ Reaction. This reaction also occurs in two stages, the first being characterised by an isosbestic point at 252 mμ, and the second by one at 268 mμ. The kinetics in 10% aqueous ethanol were followed only for the second stage, and only the dependence on $[H^+]$ was investigated. At $\mu=1.0M$, $[Cl^-]=1.0M$, and at 80.8°, the rate constants with $[H^+]=1.0$, 10^{-2}, and $4\times10^{-3}M$, were 8.48, 8.25, and 8.13×10^{-5} sec.$^{-1}$, respectively.

The $PdenCl_2\rightarrow PdCl_4^{2-}$ Reaction. A two stage reaction was observed when $PdenCl_2$ was reacted with hydrochloric acid in 5 to 10% aqueous ethanol, the first being characterised by an isosbestic point at 315 mμ, and the second by points at 240 and 263 mμ. No reaction was observed unless both hydrogen and chloride ions were present.

When the first stage, in $0.9M$ hydrochloric acid, was followed to completion and a small volume of concentrated lithium chloride then added, the reaction began again and continued until a new value of A_∞ was reached which was about 20% higher. This clearly indicates that the first stage is an approach to an equilibrium mixture. At $\mu=4.4M$, the rate of approach to the equilibrium was independent of $[H^+]$ above a concentration of $1.8M$, but was first order in $[Cl^-]$. It seems reasonable to suppose that at these acidities the intermediate is the ion $Pd(enH)Cl_3$. This assumption receives strong support from measurements of the pK_a of the acid $Pt(enH)NH_3Cl_2^+$. This was prepared as the chloride salt according to Drew's method.[10] Owing to the quite rapid reaction $Pt(enH)NH_3Cl_2^+\rightarrow Pt\,en(NH_3)Cl^+ + H^+ + Cl^-$, the acidity of the solutions increases steadily, and it is not possible to perform a normal pH titration. However, a rough estimate of the value of pK_a was obtained by extrapolating the pH of the solutions back to the time of dissolution of the complex, and applying the usual equation for the pH of a weak acid. Thus for a solution which was $4\times10^{-3}M$ in complex, the pH at dissolution was 4.9 and the derived value for pK_a was 6.4. This compares with a value of about 7 for the first acid dissociation of enH_2^{2+}.

Assuming that the reaction of $Pd(enH)Cl_3$ to re-form $PdenCl_2$ is a first order reaction, the approach to equilibrium occurs by the increasing opposition of this reaction to the pseudo-first-order forward reaction. The pseudo-first-order rate constant, k_+, for the forward reaction can then be estimated from equation (i), where

$$k_+t = \frac{(A_\infty)_{obs}-A_o}{(A_\infty)_{theo}-A_o}\ln\frac{(A_\infty)_{obs}-A_t}{(A_\infty)_{obs}-A_o} \quad \text{(i)}$$

$(A_\infty)_{obs}$ is the absorbance when equilibrium is reached, $(A_\infty)_{theo}$ is the absorbance for 100% reaction, and A_t is the absorbance measured at time t during the reaction. $(A_\infty)_{theo}$ was obtained by converting the complex completely to $PdCl_4^{2-}$ and measuring the absorbance at the isosbestic point for the two species $Pd(enH)Cl_3$ and $PdCl_4^{2-}$. Approximate values for the equilibrium constant were calculated from equation (ii), where A_o is the absorbance of the reactant $PdenCl_2$ and the other terms have been defined. Values of K at 35°

$$K = \{(A_\infty)_{obs}-A_o\}/\{(A_\infty)_{theo}-(A_\infty)_{obs}\}[Cl^-] \quad \text{(ii)}$$

and $\mu=4.4M$ were 15.9, 9.1, and 13.5 l.mole^{-1}, when $[Cl^-]=0.9$, 2.67, and $2.67M$, and $[H^+]=4.4$, 4.4, and $1.76M$, respectively.

The kinetics were followed at 263 mμ, the isosbestic point of the second stage, and absorbance changes from ~0.1 to ~0.4 were obtained in 1 cm. cells, when $\mu=4.4M$. The rate constants are given in Table V, and the activation parameters in Table VI. At $\mu=1.0M$, the optical density change was only about 0.15 and the constants are therefore less accurate. As at $\mu=4.4M$, the reaction is independent of $[H^+]$ and roughly first order in $[Cl^-]$.

The second stage was followed at 279 mμ and at ionic strengths of 1.0 and $5.0M$. The results are shown in Figure 2. At $\mu=5.0M$ the reaction is first order in $[Cl^-]$, but shows a dependence on $[H^+]$ which decreases sharply above $[H^+]=1.0M$. Rate constants at $[H^+]=5.0M$ and $[Cl^-]=1.0M$ were obtained over a temperature range from 31 to 49°, and the activation parameters were estimated graphically (Figure 3) and

Table V. Kinetic data for the first stage of the reaction $PdenCl_2\rightarrow PdCl_4^{2-}$ in 10% aqueous ethanol (followed at 263 mμ at 35.0°; $[Complex]=7\times10^{-5}M$; absorbance changed from 0.1 to 0.4 in 1 cm. cells)

(i) $\mu=4.44M$

$[H^+]$ (*M*)	4.44	4.44 [a]	4.44 [b]	4.44	1.78	4.44
$[Cl^-]$ (*M*)	0.89	0.89	0.89	2.67	2.67	4.44
10^3k_{obs} (sec.$^{-1}$)	0.90	0.369	2.36	2.70	2.75	5.00

(ii) $\mu=1.0M$

$[H^+]$ (*M*)	1.00	1.00	0.50
$[Cl^-]$ (*M*)	1.00	0.50	1.00
10^3k_{obs} (sec.$^{-1}$)	36.0	20.5	36.0

[a] At 25.0°. [b] At 45.4°.

(10) H. D. K. Drew, *J. Chem. Soc.*, 2328 (1932).

Table VI. Kinetic parameters for reactions of some chloro-aminepalladium(II) complexes with hydrochloric acid

	μ (*M*)	ΔH^* (kcal./mole)	ΔS^* (cal. deg.$^{-1}$ mole^{-1})	$k_{25°}$ (sec.$^{-1}$)
$Pd(NH_3)Cl_3^-$	5.0	23.0	— 7.4	2.3×10^{-6}
trans-$Pd(NH_3)_2Cl_2$	1.0	22.2 [a]	— 8.9 [a]	[a] 3.7×10^{-6}
	1.0	23.0	— 4.9	6.9×10^{-6}
cis-$Pd(NH_3)_2Cl_2$	1.0	17.7 [a]	—14.3 [a]	[a] 4.8×10^{-4}
	1.0	18.0	—11.2	14.0×10^{-4}
	5.0	18.5	—12.3	10.7×10^{-4}
$PdenCl_2$	4.4	16.4	—19.4	3.4×10^{-4}
$Pd(enH)Cl_3$	5.0	20.1	— 9.5	9.3×10^{-5}
$Pd(dienH_2)Cl_3^+$	5.0	19.5	— 8.9	3.5×10^{-4}
$Pd(Et_4dienH_2)Cl_3^+$	5.0	19.1	—12.4	1.4×10^{-4}

[a] Parameters for the $[Cl^-]$-independent reaction; all other parameters are for conditions such that the reactions are first order in $[Cl^-]$ and independent of $[H^+]$, the rate constants quoted being pseudo first order rate constants at $[Cl^-]=1.0M$.

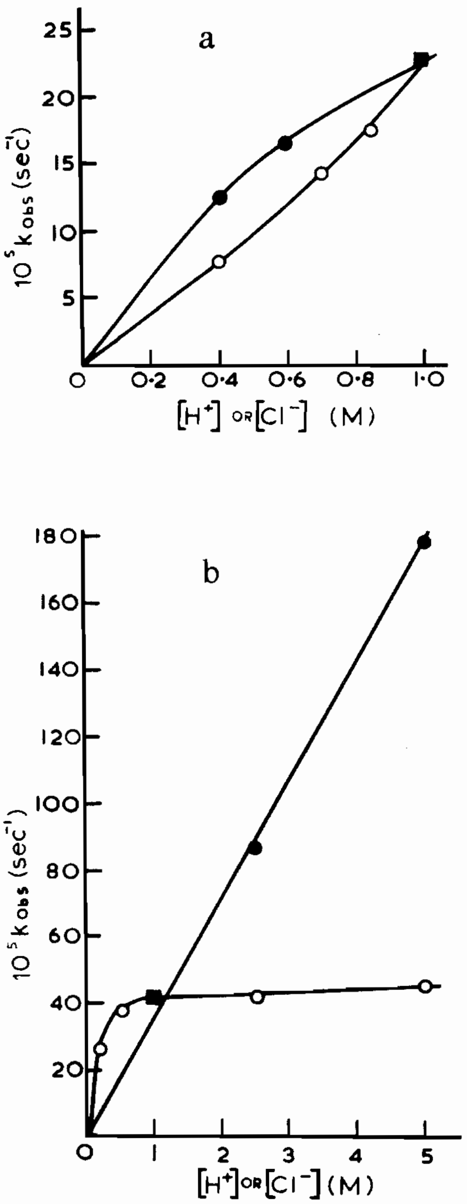


Figure 2. Rate constants for the reaction $Pd(enH)Cl_3 \rightarrow PdCl_4^{2-}$; (a) $\mu=1.0M$; ●: k_{obs} *vs.* $[H^+]$ with $[Cl^-]=1.0M$; ○: k_{obs} *vs.* $[Cl^-]$ with $[H^+]=1.0M$; ■: $[H^+]=[Cl^-]=1.0M$; (b) $\mu=5.0M$; ○: k_{obs} *vs.* $[H^+]$ with $[Cl^-]=1.0M$; ●: k_{obs} *vs.* $[Cl^-]$ with $[H^+]=1.0M$; ■: $[H^+]=[Cl^-]=1.0M$.

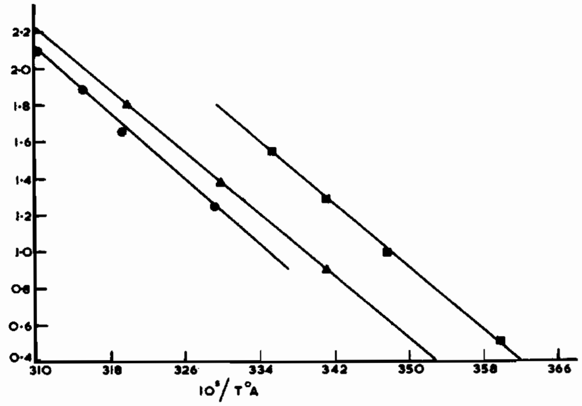


Figure 3. Arrhenius plots for the reactions of $Pd(enH)Cl_3$ (●); $Pd(dienH_2)Cl_3^+$ (■), and $Pd(Et_4dienH_2)Cl_3^+$ (△).

are given in Table VI. At $\mu=1.0M$, the dependence on $[H^+]$ is slightly less than first order, and the dependence on $[Cl^-]$ is slightly greater than first order.

The $PddienCl^+ \rightarrow PdCl_4^{2-}$ Reaction. The reaction of the Pd dienCl$^+$ ion with hydrochloric acid proceeded in two quite well defined steps, characterised successively by isosbestic points at 302 and 362 mμ, and at ~238, 261, and 356 mμ. It proved impossible to obtain unambiguous kinetic data for the first stage since increasing either $[Cl^-]$ or $[H^+]$ caused the absorbance change during the first stage to increase, and the reaction rates increased also. Unfortunately the second stage was too fast, compared with the first, for the same procedure to be followed as was used for the $PdenCl_2$ reaction. As a result only the kinetics of the second stage were followed. This is accompanied by a steady growth of the spectrum of the $PdCl_4^{2-}$ ion, and the reaction was followed at 279 mμ and at $\mu=1.0$ and 5.0*M*. Neither reaction proceeded unless both hydrogen and chloride ions were present.

At $\mu=1.0M$, the reaction is first order in $[H^+]$ and greater than first order in $[Cl^-]$ (Figure 4), whereas at $\mu=5.0M$ and $[Cl^-]=1.0M$, the observed rate constants rise to a limiting value as the value of $[H^+]$ is increased. For these studies involving variation of $[H^+]$ it proved necessary to use lithium chloride and perchlorate, rather than the sodium salts. Poor rate plots were obtained with the latter, and the approximate rate constants obtained were some 40% higher than the more accurate ones obtained using the lithium salts. Such effects are

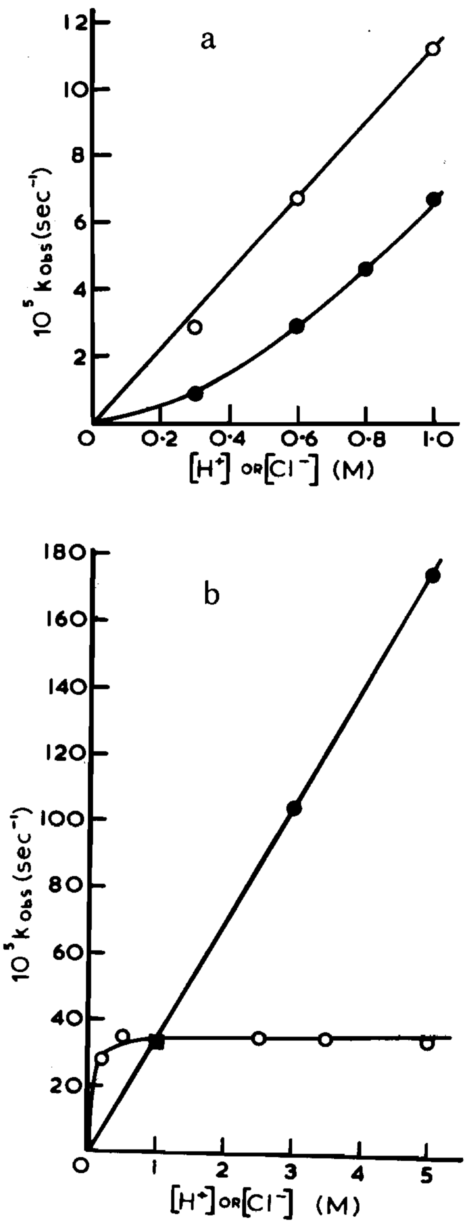


Figure 5. Rate constants for the reaction $Pd(Et_4dienH_2)_3Cl_3^+ \rightarrow PdCl_4^{2-}$; (a) $\mu = 1.0M$; ○: k_{obs} *vs.* $[H^+]$ with $[Cl^-] = 1.0M$; ●: k_{obs} *vs.* $[Cl^-]$ with $[H^+] = 0.6M$; (b) $\mu = 5.0M$; ○: k_{obs} *vs.* $[H^+]$ with $[Cl^-] = 1.0M$; ●: k_{obs} *vs.* $[Cl^-]$ with $[H^+] = 1.0M$; ■: $[H^+] = [Cl^-] = 1.0M$.

well known, especially at these high ionic strengths, and arise because the activity coefficients of the lithium ion are much closer to those of the hydrogen ion than are those of the sodium ion.[11] The dependence on $[Cl^-]$ is first order, and rate constants with $[Cl^-] = [H^+] = 5.0M$ were measured between 5 and 25° in order to obtain the activation parameters (Figure 3) which are given in Table VI.

The $PdEt_4dienCl^+ \rightarrow PdCl_4^{2-}$ Reaction. This reaction also went in two stages, the first characterised by isosbestic points at 240 and 261 mμ, and the second by points at 233 and 262 mμ. The absorbance change during the first stage was too small for accurate kinetic measurements to be possible, but the second showed clearly the growth of the spectrum of the $PdCl_4^{2-}$ ion, and the kinetics in solutions of ionic strength 1.0 and 5.0*M* were followed at 279 mμ. The results are shown in Figure 5. At $\mu = 1.0M$ and $[Cl^-] = 1.0M$, the rate increased with $[H^+]$, appearing to approach a limiting rate. At $[H^+] = 1.0M$ the reaction was first order in $[Cl^-]$. At $\mu = 5.0M$ and $[Cl^-] = 5.0M$, the reaction was slightly faster at $[H^+] = 5.0M$ than at $[H^+] = 2.0M$ ($k_{obs} = 5.36$ and 4.78, $\times 10^{-4}$ sec.$^{-1}$, respectively).

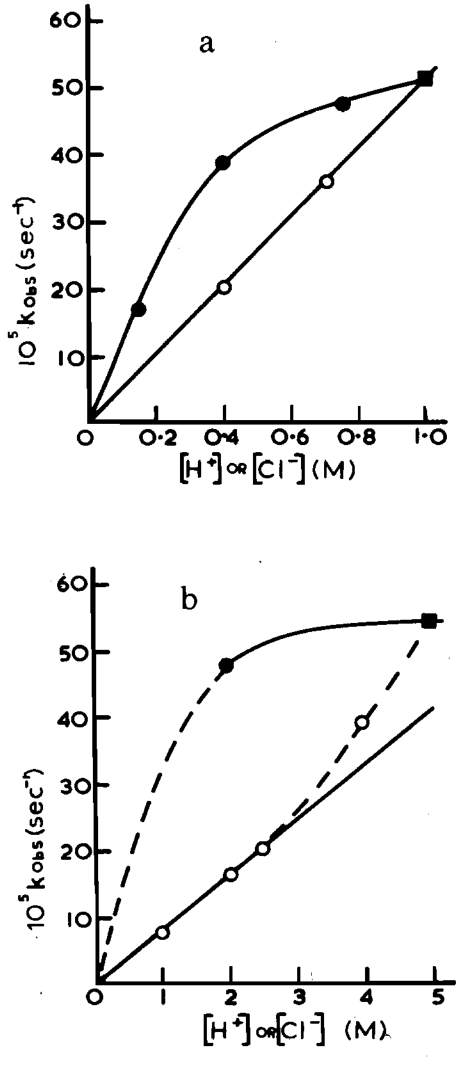


Figure 5. Rate constants for the reaction $Pd(Et_4dienH_2)Cl_3^+ \rightarrow PdCl_4^{2-}$; (a) $\mu = 1.0M$; ○: k_{obs} *vs.* $[Cl^-]$ with $[H^+] = 1.0M$; ●: k_{obs} *vs.* $[H^+]$ with $[Cl^-] = 1.0M$; ■: $[H^+] = [Cl^-] = 1.0M$; (b) $\mu = 5.0M$; ○: k_{obs} *vs.* $[Cl^-]$ with $[H^+] = 5.0M$; ●: $[H^+] = 2.0M$, $[Cl^-] = 5.0M$; ■: $[H^+] = [Cl^-] = 5.0M$.

The dependence on $[Cl^-]$ was first order up to $[Cl^-] = 2.5M$, above which the dependence seemed to rise

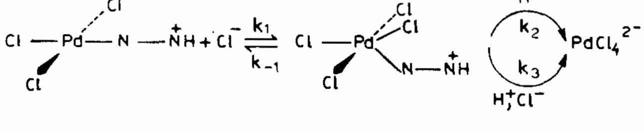
(11) R. Parsons, «Handbook of Electrochemical Constants», Butterworths, London (1959).

slightly. Activation parameters (Table VI) were estimated graphically (Figure 3) from rate constants at 20, 30 and 39.4° with $[Cl^-]=1.0M$ and $[H^+]=5.0M$.

Discussion

The results indicate a clear distinction between the behaviour of the chelated and the non-chelated complexes. The latter show a dependence on $[Cl^-]$ typical of planar d^8 complexes,[1] and this may be taken to indicate a mixture of nucleophilic attack on the metal ion by chloride and solvent. The lack of dependence on $[H^+]$, even when this is as low as about $10^{-3}M$ in some cases, suggests that the role of the hydrogen ion may be only to neutralise the ammonia or amine released, and so ensure that the reaction goes to completion.

The behaviour of the chelated complexes is notably different, the most striking features being the two stage nature of the reaction of even the $PdenCl_2$ complex, and the dependence on $[H^+]$ of the second stage of this reaction. Although a similar dependence on $[H^+]$ is found for other chelated complexes, this arises from the choice which the intermediate monodentate ligand has, either to become bidentate again by re-forming the chelate ring, or to react with hydrogen ion and rapidly dissociate from the complex altogether. This choice is not available to a complex such as $Pd(enH)Cl_3$ which contains initially only a monodentate amine, the non-complexed nitrogen atom of which is protonated at the high acidities used. The dependence on $[H^+]$ is purely kinetic, and cannot be explained in terms of a displacement of the dissociation equilibrium because the reaction goes to completion even at low acidities where the rates are much less than the limiting ones. A transition state must be involved which contains one more hydrogen ion than the reactant complex. The first order dependence on $[Cl^-]$ operates when the hydrogen ion concentration is high enough to produce the limiting rate but, when it is not so high, the dependence on $[Cl^-]$ becomes greater than first order, although it is not as great as second order. These facts can be explained by the reaction scheme (1) which leads to the rate law given in equation (iii). $N\text{-}NH^+$ represents the monodentate polyamine with the non-coordinated nitrogen atom or atoms protonated. The reaction scheme, though quite simple, incorporates two



$$k_{obs}=k_1[Cl^-]\ \frac{\{k_2[H^+]/k_{-1}+k_3[H^+][Cl^-]/k_{-1}\}}{1+k_2[H^+]/k_{-1}+k_3[H^+][Cl^-]/k_{-1}} \qquad \text{(iii)}$$

unusual features in addition to those which are currently receiving wide acceptance.[1] The latter are, briefly, that substitution reactions of square planar complexes proceed *via* the formation of a five-coordinate trigonal bipyramidal intermediate, which then decomposes to form the four coordinate product. Systematic studies of the effects of different entering and leaving groups, and of the effect of different leaving groups on the entering group dependence, have suggested that the stability of the five-coordinate intermediate varies with metal ion in the order Au(III)<Pt(II)<Rh(I).[12] For Au(III) complexes the intermediate species may well be the transition state rather than an intermediate, whereas with Rh(I) the formation and decomposition of the intermediate are two kinetically distinguishable reactions.[12]

In the series of chelated palladium(II) complexes studied here, the stability of the five-coordinated intermediate, formed during the loss of the monodentate protonated amine in the last stage of the reaction, is such that attack by a hydrogen ion is necessary in order for the forward reaction to compete with re-formation of the original four coordinate complex. The source of this stability could lie in hydrogen bonding between a hydrogen ion, joined to a non-coordinated nitrogen atom, and a coordinated chloride ion. The forward reaction could then be envisaged as an electrophilic attack by a hydrogen ion on the last coordinated nitrogen atom. If the $[H^+]$ concentration is not sufficient to produce the limiting rate, then an additional path for the forward reaction is provided which includes some assistance from an additional chloride ion. The nature of this path is by no means clear, but it is possible that, instead of intramolecular hydrogen bonding, hydrogen bonding to a free chloride ion could occur so as to form an ion pair of the type $[Cl_4Pd\text{-}N\text{-}NH^+ . Cl^-]^{2-}$ which might be more susceptible to electrophilic attack by hydrogen ion at the coordinated nitrogen atom.

A consideration of the dependence of k_{obs} on $[H^+]$ and $[Cl^-]$ at $\mu=1.0M$, allows estimates to be made of the values of the parameters k_1, k_2/k_{-1}, and k_3/k_{-1}. Thus, with $[Cl^-]$ constant at $1.0M$, the variation of k_{obs} with $[H^+]$ leads to values of k_1 and $(k_2/k_{-1}+k_3/k_{-1})$. With $[H^+]$ constant, a plot of $\{k_{obs}/[Cl^-]\}/\{k_1—k_{obs}/[Cl^-]\}$ against $[Cl^-]$ leads to values of k_2/k_{-1} and k_3/k_{-1} separately. For the reaction of $Pd(enH)Cl_3$, the values of $(k_2/k_{-1}+k_3/k_{-1})$ obtained in the two different ways are 0.88 and 0.86. For the reaction of $Pd(Et_4dienH_2)Cl_3^+$, k_{obs} is first order in $[Cl^-]$ and so $k_3 \ll k_2$. The values of k_2/k_{-1} from variation of k_{obs} with $[H^+]$ and with $[Cl^-]$ are 1.66 and 1.49, respectively. For the $Pd(dienH_2)Cl_3^+$ reaction, k_1 is not obtainable directly because k_{obs} is first order in $[H^+]$ all the way up to $[H^+]=1.0M$, but values of $k_1(k_2/k_{-1}+k_3/k_{-1})$ can be obtained in both ways and are each equal to 1.1×10^{-4} l.mole^{-1} sec.$^{-1}$.

The values derived for these parameters are given in Table VII. The value of k_1 for $Pd(enH)Cl_3$ compares with a value of 4.5×10^{-4} l.mole^{-1} sec.$^{-1}$ obtained at $\mu=5.0M$, so the reaction of this uncharged complex with chloride is unaffected by ionic strength over this range. The value of k_1 for $Pd(Et_4dienH_2)Cl_3^+$ compares with a value of 2.4×10^{-4} l.mole^{-1} sec.$^{-1}$ obtained at $\mu=5.0M$, so this positively charged complex reacts

(12) L. Cattalini, A. Orio, R. Ugo and F. Bonati, *Chem. Comm.*, 48 (1967); L. Cattalini, A. Orio and M. L. Tobe, *J. Amer. Chem. Soc.*, 89, 3130 (1967).

Table VII. Values of the rate constants for the reactions of the complexes $PdLCl_3$ with hydrochloric acid according to reaction mechanism 1 ($\mu = 1.0M$)

Complex	T (°C)	k_1 (l.mole^1 sec.$^{-1}$)	k_2/k_{-1} (l.mole^{-1})	k_3/k_{-1} (l^2.mole^{-2})	k_3/k_2 (l.mole^{-1})
$Pd(enH)Cl_3$	40.0	4.8×10^{-4}	0.52	0.34	0.65
$Pd(dienH_2)Cl_3^+$	28.7	$(6\ \times10^{-4})$	(0.05)	(0.14)	3.2
$Pd(Et_4dienH_2)Cl_3^+$	30.0	8.6×10^{-4}	1.5	<0.1	<0.1

[The values in parentheses are estimated by assuming that k_1 for the $Pd(dienH_2)Cl_4^+$ ion is affected by ionic strength in the same way as k_1 for $Pd(Et_4dienH_2)Cl_4^+$.]

more slowly with chloride at the higher ionic strength. If we assume that the reaction of $Pd(dienH_2)Cl_3^+$ is affected to the same extent by changes in ionic strength then the numbers given in parentheses in Table VII are obtained. The ratio k_3/k_2 is not dependent on this assumption.

These results show that the five-coordinate complex $Pd(dienH_2)Cl_4$ is least susceptible to attack by H^+, relative to loss of chloride, while $Pd(Et_4dienH_2)Cl_4$ is most susceptible. Just as $Pd(enH)Cl_4^-$ is more susceptible to attack by H^+, relative to loss of chloride, than is $Pd(dienH_2)Cl_4$, so is it more susceptible to the combined effects of H^+ and Cl^-, although the latter effect is smaller. In view of the lack of detailed understanding of the unusual mechanism of these reactions it would be premature to attempt a rationalisation of these trends.

In the case of the non-chelated complexes, the lack of dependence on $[H^+]$, even down to very low concentrations, suggests that the five-coordinate intermediate is much less stabilised, the type of hydrogen bonding described above not being available, and the forward reaction of the intermediate may not even need the assistance of a hydrogen ion at all. The difference in the form of the kinetic behaviour between the chelating and non-chelating amines is clearly not due to the inductive effect of the alkyl groups, necessarily present in the chelating ligands, since the *trans*-$Pd(Et_2NH)_2Cl_2$ complex behaves just like the ammine complexes in regard to $[H^+]$ dependence. The fact that the diethylamine complex reacts so much more slowly than the corresponding ammonia complex is, however, most probably due to this inductive effect.

As far as the first stages of the reactions of the chelated complexes are concerned, the absence of any kinetic data makes a detailed analysis impossible. The fact that the first stages are not easily driven to completion shows, not unexpectedly, that the five-coordinate intermediates such as $PdenCl_3^-$ return to the four-coordinate reactant much more readily than does $Pd(enH)Cl_4^-$.

The observation that only two stages were detected for the *dien* and *Et$_4$dien* complexes is surprising. The close resemblance of the second stages of reaction of these complexes, both to each other and to that of the *en* complex, strongly suggests that these reactions involve the dissociation of the last coordinated nitrogen atom as is implied in Table VI. It does not seem possible, from the data in Table VI, to decide whether it is a terminal or central nitrogen atom of the tri-amines which is the last to leave. No initial very fast reaction was observed, and the first stages are both characterised by isosbestic points. It cannot be certain that the first stage corresponds to a slow reversible dissociation of the first coordinated nitrogen atom, followed by a rapid reversible dissociation of the second, since the dissociation of the first nitrogen might be rapid but thermodynamically very unfavourable. Although the spectrum of the product of the first stage is very similar to that of the complex $PdenCl_2$, this is not significant since the first stage of the reaction of the latter complex is not accompanied by any gross changes in the shape of the spectrum, but only by an increase in the absorbance.

The kinetic behaviour of the sample assumed to be *cis*-$Pd(NH_3)_2Cl_2$ is entirely consistent with this assignment. Although some *trans* isomer might be present in small amounts, this would not affect the kinetics. Thc kinetic parameters for the complexes $Pd(NH_3)Cl_3^-$, and *cis*- and *trans*-$Pd(NH_3)_2Cl_2$, can be discussed in terms of the relative kinetic *cis*- and *trans*-effects of ammonia and chloride. After correcting for statistical effects, the rate constant for removal of ammonia from $Pd(NH_3)Cl_3^-$ is about the same as that for removal of ammonia from *trans*-$Pd(NH_3)_2Cl_2$. This *trans*-effect is about half as big as that measured by the replacement of chloride by water in platinum(II) ammine complexes.[13] The enthalpy difference is not significant in view of the precision of the data. A similarly close *trans*-effect of chloride and ammonia is found in the *trans*-Rh en_2LX^{n+} complexes (when measured in terms of enthalpies of activation).[14] The removal of ammonia from *cis*-$Pd(NH_3)_2Cl_2$ is about 60 times as easy as its removal from $Pd(NH_3)Cl_3^-$ so that in palladium(II) the *cis*-effect of ammonia is very much greater than that of chloride, when measured by this particular reaction, in contrast to the corresponding platinum(II) complexes where the *cis*-effect of ammonia is only about twice that of chloride.[13] The *cis*-effect of ammonia in the palladium(II) system is also very large when measured by the enthalpies of activation, a difference of almost 5 kcal./mole being involved. The enthalpies of activation for the complexes $PdenCl_2$ and $Pd(enH)Cl_3$ suggest that a similar *cis*-effect may be operating here, although it is not shown to such a great extent by thc rate constants. In the reactions of some platinum(II) complexes with ammonia the *cis*-effect of ammonia is greater than that of chloride only to the extent of 1.6 kcal./mole in the activation enthalpies, or a factor of 5.7 in the rate constants.[15] It is evident from these results, as well as from earlier ones,[2] that transmitted effects, whether to *cis* or to *trans* ligands, can be just as great or greater in palladium(II) complexes as in those of platinum(II).

(13) M. A. Tucker, C. B. Colvin and D. S. Martin Jr., *Inorg. Chem.*, 3, 1373 (1964).
(14) A. J. Poë and K. Shaw, *Chem. Comm.*, 52 (1967).
(15) A. A. Grinberg, *Russ. J. Inorg. Chem.*, 4, 683 (1959).

The relative importance of the [Cl⁻]-dependent path (i.c. k_2/k_1) is roughly the same for the uncharged diammine complexes but considerably less for the negatively charged monoammine. The occurrence of the [Cl⁻]-dependent path for the $Pd(NH_3)Cl_3^-$ complex is in contrast with its absence for chloride exchange[13] with $Pt(NH_3)Cl_3^-$ The importance of the [Cl⁻]-dependent term increases when the ionic strength is raised from 1.0 to 5.0*M*, possibly because of a large decrease in the activity of the solvent.

No [Cl⁻]-independent path seems to occur for any of the chelate complexes, and this is explicable if the hydrogen bonding, which stabilises the five coordinate intermediate, involves the incoming chloride ion and not one of those already coordinated, ion pairing to the uncoordinated and protonated end of the ligand provinding a favourable path for introducing the chloride into the complex.

Acknowledgment. Acknowledgment is made to the Science Research Council for the award of a research studentship to one of us (D.H.V.).