Preparation and Kinetic Study of Some Sterically Hindered Palladium(II) Complexes

W. H. **Baddley**[1] **and Fred Basolo**

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois. *Received February 17, 1966*

Abstract: The preparation and characterization of complexes of the type [Pd(N-alkyltriamine)X]X [N-alkyltriamine = 1,4,7-trimethyldiethylenetriamine (Me_3dien), 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien), and 1,1,4,-7,7-pentamethyldiethylenetriamine (Me_5dien); X = Cl, Br, I, etc.] are described. A kinetic study of the replacement of the acido group by another ligand has been carried out in aqueous solution. The gross kinetic behavior of these sterically hindered Pd(II) complexes resembles more that of octahedral systems than the kinetic characteristics of square-planar complexes. What is believed to be the first example of hydroxide ion catalysis in square-planar complexes is reported and discussed in terms of a conjugate-base mechanism.

Kinetic and mechanistic studies of substitution reactions of square-planar metal complexes have been confined primarily to those substrates containing Pt(II) as the central metal ion, and enough data has been accumulated so that the essential features of such substitutions are believed to be understood.[2] In an effort to extend such studies to other square-planar substrates, the kinetics and mechanism of substitution reactions of some Au(III) complexes were recently investigated.[3] A preliminary inquiry into the analogous Pd(II) system, $[Pd(dien)X]^+$ (dien = diethylenetriamine, $H_2NC_2H_4NHC_2H_4NH_2$), showed that substitutions of the X group by another acido group were very rapid (reactions complete in less than 0.1 sec). In order to obtain a Pd(II) system more amenable to detailed studies, attempts were directed to the preparation of some Pd(II) complexes containing N-alkylated diethylenetriamines instead of diethylenetriamine itself, since molecular models showed that in such complexes the metal atom was not so open to nucleophilic attack above and below the square plane due to the bulkiness of the alkyl groups. This paper describes the preparation and characterization of these sterically hindered Pd(II) complexes and a kinetic study of acido-substitution reactions.[4]

A second, and more general reason for the preparation of metal complexes containing bulky N-alkylated polyamines as ligands is that, when this work was started, these types of systems had been very little studied. However, since our previous communication,[4] there has been a considerable amount of research done on the preparation and properties of metal complexes of the N-substituted dien ligands.[5] Multidentate tertiary phosphine and tertiary arsine donor ligands containing bulky alkyl or aryl groups have evoked much interest in the past few years.[6] However, examples of tertiary amines bonded to transitional metal ions were rare. Examples of bidentate tertiary amine complexes are known.[7] It would be of interest to compare the stereochemistry of complexes formed from tertiary tridentate or quadridentate amine ligands with analogous complexes containing phosphine or arsine ligands because the latter ones give rise to five-coordinate complexes of Pd(II) and Pt(II).[8] If steric reasons are paramount in forcing the metals to be five coordinate for P and As ligands, then one might expect analogous behavior for tertiary amines. On the other hand, if electronic effects are more important, and since amines are not π-acceptor ligands as are phosphines and arsines, one would expect square-planar stereochemistry for the d^8 systems of Pd(II) and Pt(II) with tertiary amines. Some of the new Pd(II) complexes of tertiary tridentate amines described herein allow such a comparison to be made since analogous arsine complexes are known.

Experimental Section

Materials. The palladium-containing starting material was palladium chloride, $PdCl_2$, which was purchased from Engelhard Industries, Inc.

Diethylenetriamine (Union Carbide, technical grade) was distilled once, bp 204–208°.

From the Ames Laboratories, Milford, Conn., were obtained 1,4,7-trimethyldiethylenetriamine, 1,1,7,7-tetraethyldiethylenetriamine, and 4-methyl-1,1,7,7-tetraethyldiethylenetriamine.

From the Columbia Organic Chemicals Co., Inc., Columbia, S. C., 1,1,4,7,7-pentamethyldiethylenetriamine was obtained. These amines were used without further purification.

Preparation of Complexes. A. Complexes of Diethylenetriamine. Compounds of the type [Pd(dien)X]X (X = Cl, Br, I) were first prepared by the literature method,[9] but a more expedient method was found, which is illustrated by the preparation of the bromo complex. Two grams of $PdCl_2$ (11 mmoles) was suspended in 10 ml of water, and 2 ml of dien (20 mmoles) was added. The mixture was placed on a steam bath for 5 min, and a clear yellow solution resulted. To the warm solution was added 5 g of LiBr, and the solution was allowed to cool to room temperature. The pH of the solution was reduced to *ca.* 6 by the dropwise addition of HBr, whereupon yellow crystals began to form. These were collected on a filter and washed with water, ethanol, and ether. After air drying for 48 hr, a yield of 1.9 g was obtained, which is 50% of

---

(1) Department of Chemistry, Louisiana State University, Baton Rouge, La.

(2) For the most recent review of this subject see F. Basolo, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 81.

(3) (a) W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964); (b) C. F. Weick and F. Basolo, *ibid.*, **5**, 576 (1966).

(4) Some of the results described herein have been previously communicated: (a) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2076 (1964); (b) F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.*, 3, 1202 (1964).

(5) (a) M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966); (b) Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966).

(6) (a) L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 453 (1964); (b) G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964).

(7) F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2772 (1958).

(8) C. M. Harris and S. E. Livingstone, *Rev. Pure Appl. Chem.*, **12**, 16 (1962).

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

theory. *Anal.* Calcd for $PdC_4H_{13}N_3Cl_2$: C, 17.13; H, 4.67. Found: C, 17.50; H, 4.75. Calcd for $PdC_4H_{13}N_3I_2$: Pd, 22.96; C, 10.37; H, 2.83. Found: Pd, 23.4; C, 10.95; H, 3.12.

B. Complex of 1,4,7-Trimethyldiethylenetriamine. The compound $[Pd(Me_3dien)Br]Br$ was prepared by stirring together 1 g of $PdCl_2$ (5 mmoles), 3 ml of concentrated HCl, and 17 ml of water until the $PdCl_2$ disssolved to give a deep red solution of H_2PdCl_4. The amine was added slowly while the H_2PdCl_4 solution was stirred magnetically. After the addition of 3.8 ml of amine (19 mmoles), the original deep red color of the solution had changed to light yellow, and the pH was *ca.* 5. To this clear yellow solution was added 2 g of LiBr, and the volume of the solution was reduced to 5 ml with a rotary evaporator. An orange, oily substance remained. This material was dissolved in 25 ml of EtOH, and ether was added until a cloudiness appeared. An orange oil formed. The mixture was placed in a refrigerator, and after 12 days the oil had changed to a yellow solid. This was collected on a filter and recrystallized from 15 ml of hot EtOH. The yield was 0.4 g. *Anal.* Calcd for $PdC_7H_{19}N_3Br_2$: Pd, 26.0. Found: Pd, 26.0.

C. Complexes of 1,1,7,7-Tetraethyldiethylenetriamine. A mixture of 2 g of $PdCl_2$ (11 mmoles), 5 ml of concentrated HCl, and 15 ml of water was stirred at room temperature until the $PdCl_2$ dissolved to give a deep red solution of H_2PdCl_4. The solution was filtered, and to the filtrate was added Et_4dien slowly as the mixture was stirred magnetically. After 2 ml of amine had been added, an orange solid began to form and the color of the solution changed to orange. After 8 ml of amine had been added (pH *ca.* 6) the orange solid still remained. (This solid is presumably $[Pd(Et_4dien)Cl]_2$-$[PdCl_4]$, and in some preparations it did not appear.) The mixture was warmed on a steam bath for 5 min and the solid dissolved, resulting in a clear yellow solution. To the warm solution was added 2 g of LiCl, but no crystallization occurred as the solution was cooled to room temperature. The volume of the solution was reduced to 10 ml and a yellow solid separated. This solid was collected on a filter, washed with Et_2O, and then recrystallized from 10 ml of warm EtOH. The yield of $[Pd(Et_4dien)Cl]Cl$ was 1.0 g. *Anal.* Calcd for $PdC_{12}H_{29}N_3Cl_2$: Pd, 27.1. Found: Pd, 27.4.

Several compounds of the type $[Pd(Et_4dien)X]X$ were prepared by a metathetical reaction between an *in situ* preparation of the chloro complex and LiX or NaX, followed by recrystallization of the product from an ethanol–water mixture. Addition of LiBr gave $[Pd(Et_4dien)Br]Br$ as yellow needles. *Anal.* Calcd for $PdC_{12}H_{29}N_3Br_2$: Pd, 22.09; C, 29.92; H, 6.06. Found: Pd, 22.4; C, 30.08; H, 6.43. Treatment of the *in situ* preparation of $[Pd(Et_4dien)Cl]Cl$ with NaI gave a brownish gold solid, $[Pd(Et_4dien)I]I$, after recrystallization from warm EtOH. *Anal.* Calcd for $PdC_{12}H_{29}N_3I_2$: Pd, 18.5. Found: Pd, 19.3. The use of NaN_3 gave a product of orange crystals, which presumably was $[Pd(Et_4dien)N_3]N_3$ although it was not analyzed. Addition of $NaNO_2$ to a solution of $[Pd(Et_4dien)Cl]Cl$, followed by acidification to a pH of *ca.* 7 with $HClO_4$, yielded a substance which was very insoluble in water, and it was not studied further. When KSCN was added to the yellow solution of $[Pd(Et_4dien)Cl]Cl$, the color changed to a lighter yellow, and after sitting in an ice bath for 30 min, yellow crystals of $[Pd(Et_4dien)NCS]SCN$ began to form. The solid was collected on a filter and recrystallized from a warm 1:1 mixture of ethanol and water. The infrared absorption spectrum shows a band at 832 cm^{-1} which is not present in the corresponding bromo complex. *Anal.* Calcd for $PdC_{14}H_{29}N_5S_2$: C, 38.39; H, 6.67. Found: C, 38.59; H, 6.63. The S-bonded linkage isomer, $[Pd(Et_4dien)SCN]SCN$, was prepared by a different procedure.[10] Acetone (10 ml) was cooled in an ice–salt bath; then 0.5 g of $K_2[Pd(SCN)_4]$ (1.2 mmoles) was dissolved therein. To this solution was added 0.3 ml of Et_4dien, which also had been cooled to 0°, and the color of the solution changed to light orange. An additional 0.2 ml of amine was added, and the color changed to light yellow. The acetone was removed with a rotary evaporator, the flask being immersed in an ice–salt bath during the process. The yellow solid which remained was washed from the flask with small portions of ice water and collected on a filter where it was washed with ethanol and ether. An infrared spectrum was taken immediately and the presence of a weak band at 710 cm^{-1} and the absence of a band at 832 cm^{-1} suggest that the complex is S bonded. Four months later an infrared spectrum of the material was recorded; the band at 710 cm^{-1} had disappeared, and a new band at 832 cm^{-1} was present. These data indicate that the S-bonded complex had isomerized in the solid state to the N-bonded form sometime during the 4-month period.

D. Complex of 1,1,4,7,7-Pentamethyldiethylenetriamine. Attempts to prepare complexes of Pd(II) with Me_5dien yielded only oils until the following precedure was tried. One gram of $PdCl_2$ (5.6 mmoles), 1 ml of concentrated HCl, and 40 ml of water were refluxed for a few minutes until complete solution of $PdCl_2$ occurred. To the hot solution was added 1.5 ml of Me_5dien (8.7 mmoles), and the mixture was refluxed until an orange solution resulted. The mixture was filtered and the clear, orange filtrate (pH *ca.* 2) was placed on a steam bath to reduce the volume. Small amounts of Li_2CO_3 were added occasionally to prevent the solution from becoming too acidic. When this occurred, the color changed to deep orange indicating presumably the formation of $PdCl_4^{2-}$ in solution. Evaporation was continued until only a sticky substance remained. This material was dissolved in 50 ml of ethanol, and to the solution was added 10 ml of water containing 1.0 g of NH_4PF_6. Yellow crystals of $[Pd(Me_5dien)Cl]PF_6$ separated as the solution cooled. These were collected on a filter, washed well with EtOH, and recrystallized from a hot ethanol–water mixture. *Anal.* Calcd for $PdC_9H_{23}N_3ClPF_6$: C, 23.49; H, 5.04. Found: C, 23.63; H, 5.00.

E. Complex of 4-Methyl-1,1,7-tetraethyldiethylenetriamine. The complex $[Pd(MeEt_4dien)Cl]PF_6$ was prepared by Mr. Gary Haller using a procedure analogous to that described above for the Me_5dien complex. *Anal.* Calcd for $PdC_{13}H_{31}N_3ClPF_6$: C, 30.2; H, 6.0. Found: C, 30.6; H, 6.0.

Analyses. Carbon and hydrogen analyses were performed by Micro-Tech Laboratories, Skokie, Ill. In some of the compounds the palladium content was determined by ignition.

Conductivity Measurements.. These were made with an Industrial Instruments, Inc., conductivity bridge, Model RC 16B1. The conductivity cell was of the dip type manufactured by Industrial Instruments, Inc.

Spectra. Visible and ultraviolet spectra were measured on Beckman DK-2 and Cary 14 spectrophotometers in 1-cm quartz cell. Infrared spectra were measured with a Beckman IR-5 instrument by mulling the sample in Nujol.

Kinetic Studies. Reactions indicated by eq 1–4 were studied in aqueous solution at 25°

$$[Pd(dien)X]^+ + Y^- \longrightarrow [Pd(dien)Y]^+ + X^- \qquad (1)$$

$$X = Cl, Br, I;\ Y = Br, I, SCN, N_3, OH, \text{thiourea}$$

$$[Pd(Me_5dien)X]^+ + Y^- \longrightarrow [Pd(Me_5dien)Y]^+ + X^- \qquad (2)$$

$$X = Cl;\ Y = I, N_3, OH, \text{thiourea}$$

$$[Pd(Et_4dien)X]^+ + Y^- \longrightarrow [Pd(Et_4dien)Y]^+ + X^- \qquad (3)$$

$$X = Cl, Br;\ Y = Br, I, SCN, NO_2, N_3, OH$$

$$[Pd(MeEt_4dien)X]^+ + Y^- \longrightarrow [Pd(MeEt_4dien)Y]^+ + X^- \qquad (4)$$

$$X = Cl;\ Y = Br, N_3, OH$$

A spectrophotometric method was used in all cases. Reaction 1, which is very fast (complete in less than 0.1 sec), was studied with a stopped-flow apparatus as was reaction 2, which is slower (complete in *ca.* 10 sec). Reactions 3 and 4 were followed with either a Beckman DK-2, Beckman DU, or Cary 14 spectrophotometer. Pseudo-first-order conditions were employed in which the concentration of reagent was at least ten times the substrate concentration. The rate constants were obtained graphically from the usual first-order plot.

Evidence that the reactions being followed kinetically were, in fact, those listed above comes from the observation of isosbestic points during the course of the reaction and, in some cases, spectrophotometric identification of the products. For reaction 3, in particular, several of the products were synthesized and the ultraviolet spectrum of an aqueous solution of the pure compound was compared with the spectrum of the reaction mixture after it had gone to completion. Such a comparison for several of the reactions is shown in Table I. Also, Figure 1 shows the change in the absorption spectrum as a function of time for one of the reactions.

As will be reported in the Results section, complexes of the type [Pd(amine)Cl]Cl where "amine" is dien, Et_4dien, $MeEt_4dien$, or Me_5dien appear to be partially hydrolyzed in aqueous solution.

$$[Pd(amine)Cl]^+ + H_2O \rightleftarrows [Pd(amine)H_2O]^{2+} + Cl^- \qquad (5)$$

However, since it is well known that substitution reactions of aquo complexes of Pt(II) proceed at a considerably faster rate than for

---

[10] F. Basolo, W. H. Baddley, and K. J. Weidenbaum, *J. Am. Chem. Soc.*, **88**, 1576 (1966).

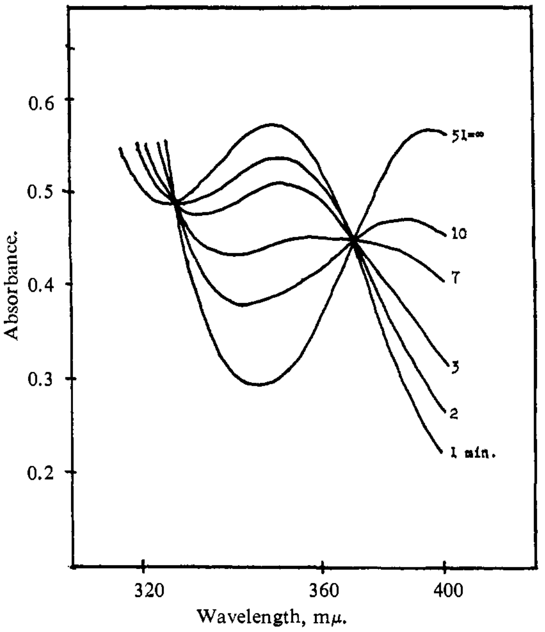


Figure 1. Spectral changes during the reaction of $[Pd(Et_4dien)Cl]^+$ (8×10^{-4} *M*) with iodide ion (8×10^{-2} *M*) in water at 25°.

acido complexes,[11] it is felt that a small quantity of the aquo complex in the substrate reaction solution did not alter the kinetic results. The stoichiometric reactions that were proceeding in a kinetic run, with the chloro complex as substrate, are given by

$$[Pd(amine)Cl]^+ + H_2O \rightleftharpoons [Pd(amine)H_2O]^{2+} + Cl^- \qquad (6)$$

$$[Pd(amine)H_2O]^{2+} + Y^- \longrightarrow [Pd(amine)Y]^+ + H_2O \qquad (7)$$

$$[Pd(amine)Cl]^+ + Y^- \longrightarrow [Pd(amine)Y]^+ + Cl^- \qquad (8)$$

The fact that isosbestic points were observed for most of the reaction indicates that reaction 7 was complete very quickly. Generally, for a reaction whose half-life was *ca.* 5 min, isosbestic points were not good for the first minute of the reaction when reagents such as bromide, iodide, thiocyanate, and azide ions were present. For hydroxide ion, however, the reaction showed perfect isosbestic points from the first reading to the last. This observation is consistent with the above-mentioned scheme, since reaction 7, in the case of hydroxide as reagent, involves merely a proton transfer and was therefore complete before the first spectrum could be taken.

Table I. Spectral Identification of Products of Reaction

$$[Pd(Et_4dien)Cl]^+ + Y^- \xrightarrow[H_2O]{25°} [Pd(Et_4dien)Y]^+ + Cl^-$$

	—Reaction product—		—Pure compound—	
Y	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
Br	358	710	358	690
I	395	615	387	654
SCN	325	1380	325	1360
N_3	320	1720	320	1780

Results

The new compounds prepared in this study are listed in Table II along with color, conductivity, and spectrophotometric data. The complex $[Pd(Et_4dien)Cl]Cl$ is known to be diamagnetic.[12]

Substitution reactions of the unhindered $[Pd(dien)X]^+$ (X = Cl, Br, I) substrates were so fast that, even with a stopped-flow apparatus, very little quantitative data could be obtained. These data appear in Table III.

Table II. Properties of the New Compounds $[Pd(N\text{-alkyltriamine})X]$ Y

Compound	Color	Molar conductance[a]	—Ultraviolet— λ_{max}, mμ	ϵ_{max}
$[Pd(Me_3dien)Br]Br$	Yellow	...	...	...
$[Pd(Et_4dien)Cl]Cl$	Yellow	121	346[c]	815[c]
$[Pd(Et_4dien)Br]Br$	Yellow	...	358[d]	690[d]
$[Pd(Et_4dien)I]I$	Old gold	101	387	654
$[Pd(Et_4dien)N_3]N_3$	Orange	...	320	1780
$[Pd(Et_4dien)NCS]SCN$	Pale yellow	91	325[e]	1360[e]
$[Pd(Et_4dien)SCN]SCN$	Yellow	...	...	...
$[Pd(Me_5dien)Cl]PF_6$	Yellow	136[b]	339[f]	775[f]
$[Pd(MeEt_4dien)Cl]PF_6$	Yellow	120	348[g]	785[g]

[a] These values are given in $ohm^{-1}\ cm^{-2}\ mole^{-1}$ and were measured in 10^{-3} *M* aqueous solutions at room temperature. [b] A value of 28 $ohm^{-1}\ cm^{-2}\ mole^{-1}$ was obtained in nitrobenzene where values of *ca.* 30 $ohm^{-1}\ cm^{-2}\ mole^{-1}$ are usually observed for 1:1 electrolytes. [c] In the presence of 0.1 *M* chloride the absorption maximum shifted to 348 mμ (ε 860). [d] The absorption maximum shifted to 360 mμ (ε 755) in the presence of 0.5 *M* bromide. [e] The spectrum was identical in the presence of 0.1 *M* thiocyanate. [f] The absorption maximum shifted to 348 mμ (ε 805) in the presence of 0.1 *M* chloride. [g] The absorption shifted to 355 mμ (ε 775) in the presence of 0.1 *M* chloride.

Table III. Experimental First-Order Rate Constants for Reactions of $[Pd(dien)X]^+$ with Various Nucleophiles (Y) in Water at 25°

X	[Y], *M*	k_{obsd}, sec^{-1}
Cl	OH^-; pH 10 buffer	...[a]
Br	0.01 OH^-	45
Br	0.04 OH^-	50
Br	0.01 I^-	...[a]
I	0.027 thiourea	...[a]
I	0.005 OH^-	10
I	0.026 OH^-	11
I	0.053 OH^-	12
I	0.100 OH^-	14
I	0.001 SCN^-	...[a]

[a] These reactions were complete in less than 0.1 sec, and, with the stopped-flow apparatus at our disposal, rate constants could not be evaluated.

Experiments were carried out with the slightly hindered $[Pd(Me_3dien)Br]^+$ substrate, and the rate of bromide replacement was generally about the same as that for the unhindered complex, $[Pd(dien)Br]^+$. For example, the reaction of $[Pd(Me_3dien)Br]^+$ with iodide ion was too fast to measure at 25°. No quantitative data were obtained for this system, although for some of the reagents, *e.g.*, hydroxide ion, the rates of reaction were probably slow enough to measure by the stopped-flow method.

The substrate $[Pd(Me_5dien)Cl]^+$ reacted with several reagents about 300-fold slower than $[Pd(dien)Cl]^+$. Results are tabulated in Table IV.

More drastic steric hindrance, as in complexes of the type $[Pd(Et_4dien)X]^+$, decreased the rates of the substitution reactions remarkably. Rate constants given in Tables V and VI show that this substrate reacted with all reagents studied, except hydroxide ion, by a process which is independent of the reagent concentration. Data are plotted for the chloro complex in Figure 2.

---

(11) H. B. Gray and R. Olcott, *Inorg. Chem.*, 1, 481 (1962).
(12) We thank Professor H. B. Gray for this measurement.

Table IV. Experimental First-Order Rate Constants for Reactions of $[Pd(Me_5dien)Cl]^+$ with Various Nucleophiles (Y) in Water at 25°

[Y], *M*	k_{obsd}, sec^{-1}
0.0106 Br^-	0.25
0.0201 Br^-	0.24
0.0403 Br^-	0.25
0.0103 OH^-	0.32
0.099 OH^-	0.31
0.011 thiourea	0.26
0.038 thiourea	0.30
0.076 thiourea	0.35
0.025 N_3^-[a]	0.28
0.049 N^{3-}	0.28
0.099 N^{3-}	0.31

[a] The sodium azide solutions had added to them sufficient $HClO_4$ to make the pH *ca.* 5.5.

Table V. Experimental First-Order Rate Constants for Reactions of $[Pd(Et_4dien)Cl]^+$ with Various Nucleophiles (Y) in Water at 25°

[Y], *M*	$k_{obsd.}$ sec^{-1}
0.0137 Br^-	0.0021
0.0275 Br^-	0.0021
0.038 Br^-	0.0022[a]
0.099 Br^-	0.0022[b]
0.0078 I^-	0.0019
0.010 I^-	0.0019[c]
0.078 I^-	0.0022
0.10 I^-	0.0020[d]
0.039 I^-	0.00087[e]
0.039 I^-	0.0046[f]
0.039 I^-	0.0020[g]
0.007 N_3^-	0.0026[h]
0.087 N_3^-	0.0033[h]
0.017 N_3^-	0.0024[i]
0.034 N_3^-	0.0025[i]
0.034 SCN^-	0.0020
0.068 SCN^-	0.0021
0.00495 OH^-	0.0025
0.0133 OH^-	0.0030
0.0263 OH^-	0.0035
0.0535 OH^-	0.0052

[a] 0.16 *M* $LiClO_4$. [b] 0.10 *M* $LiClO_4$. [c] 0.19 *M* $LiClO_4$. [d] 0.10 *M* $LiClO_4$. [e] At 14.3°. [f] At 36.5°. [g] At 25.0°. [h] Phosphate buffer, pH 7. [i] pH 5.5 with $HClO_4$.

Table VI. Experimental First-Order Rate Constants for Reactions of $[Pd(Et_4dien)Br]^+$ with Various Nucleophiles (Y) in Water at 25°

[Y], *M*	k_{obsd}, sec^{-1}
0.010 I^-	0.0013
0.020 I^-	0.0016
0.30 I^-	0.0014
0.080 I^-	0.0015
0.0039 N_3^-	0.0013[a]
0.0196 N_3^-	0.0016[a]
0.0392 N_3^-	0.0017[a]
0.010 NO_2^-	0.0014[a]
0.049 NO_2^-	0.0014[a]
0.078 NO_2^-	0.0015[a]
0.100 NO_2^-	0.0014[a]
0.004 SCN^-	0.0012
0.040 SCN^-	0.0013
0.0039 OH^-	0.0017
0.010 OH^-	0.0019
0.020 OH^-	0.0025
0.043 OH^-	0.0037

[a] Phosphate buffer; pH *ca.* 7.

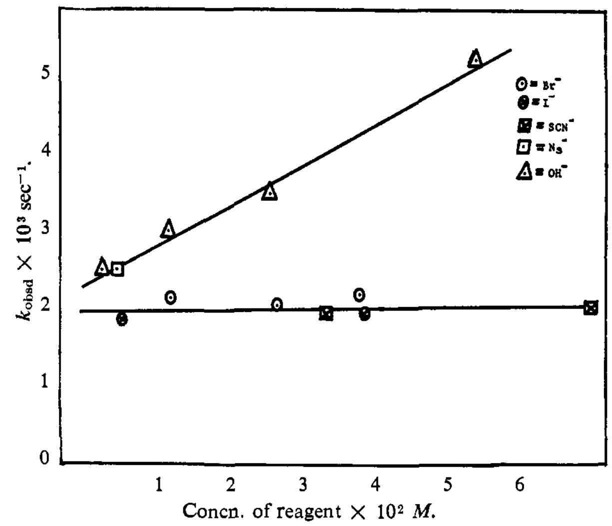


Figure 2. Plot of k_{obsd} *vs.* reagent concentration for reactions of $[Pd(Et_4dien)Cl]^+$ with various nucleophiles in water at 25°.

Finally, substitution reactions of $[Pd(MeEt_4dien)Cl]PF_6$ were studied kinetically. These results are given in Table VII.

Table VII. Experimental First-Order Rate Constants for Reactions of $[Pd(MeEt_4dien)Cl]^+$ with Various Nucleophiles (Y) in Water at 25°

[Y], *M*	k_{obsd}, sec^{-1}
0.014 Br^-	0.00087
0.069 Br^-	0.00086
0.133 Br^-	0.00090
0.03 OH^-	0.00074
0.046 OH^-	0.00080
0.100 OH^-	0.00073

Discussion

A. General Characteristics of [Pd(N-alkyltriamine)-X]X Complexes. Spectral, conductivity, and magnetic data of the sterically hindered palladium complexes prepared in this study are consistent with a square-planar structure, both in the solid state and in aqueous solution. The complexes show a single absorption band of medium intensity in the 300–400-mμ region, which is the same type of spectrum that has been observed for dien complexes of Pd(II), Pt(II), and Au(III),[13] all of which are presumed to be square planar. As the degree of N-alkylation increases, however, the positions and intensities of the absorption bands change in a regular fashion relative to the unhindered $[Pd(dien)X]^+$ complex. For example, the absorption maxima of $[Pd(AAA)Cl]^+$ (AAA = dien, Me_5dien, Et_4dien, and $MeEt_4dien$) occur at 330, 342, 348, and 355 mμ, respectively, with corresponding ε values of 460, 635, 860, and 775. The conductivity data (Table II) support a four-coordinate formulation in aqueous solution, the values being approximately what is expected for 1:1 electrolytes. The slightly high values (120–150 ohm^{-1} cm^{-1} $mole^{-1}$) for the chloro complexes indicate partial hydrolysis.

(13) W. H. Baddley, F. Basolo, H. B. Gray, C. Nolting, and A. J. Poe, *Inorg. Chem.*, **2**, 921 (1963).

As mentioned in the introduction, metal complexes of N-alkylated multidentate amines with the second- and third-row transition metal ions have been very little studied. It is known from stability constant determinations that complexes of N-alkylamines are less stable than complexes of the corresponding N-hydrogenamines. This instability has been attributed to steric hindrance[14] since the N-alkylamines are stronger bases and would otherwise be expected to form more stable complexes. Thus, it is not surprising that metal complexes containing coordinated bulky amines are not too numerous. Chatt and Wilkins[15] pointed out that a stable tertiary amine complex would result only if the tertiary nitrogen atom is part of a chelate ring in which the bonding of the other atoms is such that the "tertiary nitrogen atom is held so that dissociation from the metal atom is impossible." This view is certainly exaggerated because Mann and Watson[7] were able to prepare stable complexes of the ditertiary amine, N,N,N,'N'-tetramethylethylenediamine, with Pd(II) and Pt(II). However, these same authors were unable to isolate complexes of this amine with Co(III) and Rh(III), metal ions which readily form complexes with the unhindered ethylenediamine. More recently, a Au(III) complex of N,N,N',N'-tetramethylethylenediamine has been prepared[16] as has a bisamine complex of Pd(II).[17]

These sterically hindered complexes of Pd(II) containing coordinated Me_3dien, Et_4dien, $MeEt_4$dien, and Me_5dien are interesting in several respects. First of all, the compounds are stable. Solid samples in the laboratory have not altered visibly over a 2-year period. Admittedly, some of the compounds were difficult to isolate because the products of the reactions were usually more oily than crystalline. This is believed to have been due to problems related to packing of the cation and anion in the crystal, and not to an inherent instability of the complexes. Thus, to isolate the bulky cations, it was usually necessary to use a large anion. The trend observed was that the more alkyl groups on the amine, the greater was the tendency for the product to be oily.

A second point of interest concerning these complexes is that those of the type $[Pd(MeEt_4dien)Cl]PF_6$ and $[Pd(Me_5dien)Cl]PF_6$ were apparently the first examples[4] of metal complexes containing tridentate, tertiary amines as ligands. The nickel, palladium, and platinum complexes of the structurally related tritertiary arsine, bis(3-dimethylarsinopropyl)methylarsine, have been described.[18] An X-ray structure determination showed the nickel complex, $Ni(triarsine)Br_2$, to be five coordinate in a square-pyramidal arrangement, whereas the analogous Pd complex is square planar.[19] It has been recently reported that the Ni(II) complex of the tertiary amine, Me_5dien, is five coordinate.[5a] Conductivity and spectral data presented herein for the Me_5dien complex of Pd(II) indicate that this complex is square planar, as are the Pd(II) arsine complexes. With the limited data at hand, no definite conclusions may be drawn concerning the factors responsible for the stereochemistry of complexes containing analogous tritertiary amine and arsine ligands. It is interesting, however, that there is a parallel in these particular examples even though the electronic properties of the donor atoms are quite different.

A third point of interest is the "shape" of these sterically hindered complexes and the consequences that arise therefrom. As stated above, the spectral, conductivity, and magnetic data are consistent with a low-spin, square-planar structure. Molecular models show that, in such a planar arrangement, the bulky N-alkyl groups are more or less perpendicular to the square plane and occupy most of the space immediately above and below this plane. In addition, these alkyl groups exert a steric hindrance on the acido group. We have previously suggested[4b] that the mode of bonding of the thiocyanate group in the ion $[Pd(Et_4dien)NCS]^+$, *i.e.*, N bonded, is a direct result of the constrictions which arise due to the presence of the four ethyl groups. The S-bonded isomer has also been prepared, but the N-bonded complex is the thermodynamically stable form as evidenced by the fact that the S-bonded complex isomerizes to the N-bonded form in the solid state and in solution.[10] The spectacular effect of the shape of these hindered molecules on the kinetics of substitution is discussed below.

B. Kinetics and Mechanism of Substitution of Sterically Hindered Pd(II) Complexes. Extensive kinetic studies of the $[Pd(dien)X]^+$ substrates were not feasible due to the high velocity of these reactions. Several observations may be made, however. First of all, for $[Pd(dien)X]^+$ reacting with a given nucleophile, the reactivy decreases as X is varied in the order shown by (9). This order is the same one that

$$Cl > Br > I \qquad (9)$$

was previously observed for both Pd(II) and Pt(II) substrates.[9] The rate law for these reactions could not be determined for any of the reagents studied except hydroxide ion, where the rate is essentially independent of the hydroxide concentration over the range from 0.005 to 0.1 *M*. One may surmise that reactions of these Pd(II) substrates with other nucleophiles such as I^-, SCN^-, etc., are not zero order in these reagents because qualitatively the reactions were much faster than the hydroxide ion reaction. This result of zero-order hydroxide kinetics is in contrast to observations of Banerjea and Tripathi[20] who claimed that hydroxide ion reacted with complexes such as $[Pd(en)Cl_2]$ and $[Pd(NH_3)_2Cl_2]$ by an S_N2 process. It is difficult to see how these authors reached this conclusion based on their published data since every reaction they studied with hydroxide ion as a reagent was complete in less than 5 sec, and, with the conductivity procedure they were using, no rate constants could be obtained. It has been previously shown that some Pt(II) and Au(III) substrates of the type $[M(dien)X]^{n+}$ undergo base hydrolysis at a rate which is independent of the hydroxide ion concentration.[3,21] Since Pd(II) is also a d^8 system whose chemistry is very similar to Pt(II) and Au(III), it is not

---

[14] F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **76**, 211 (1954).

[15] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 4300 (1952).

[16] W. H. Baddley, Ph.D. Dissertation, Northwestern University, Evanston, Ill., 1964.

[17] D. W. Meek, *Inorg. Chem.*, **4**, 250 (1965).

[18] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961).

[19] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).

[20] D. Banerjea and K. K. Tripathi, *J. Inorg. Nucl. Chem.*, **7**, 78 (1958).

[21] H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962).

surprising that complexes of the type $[Pd(dien)X]^+$ react with hydroxide ion at a rate which is independent of the hydroxide ion concentration.

Since $[Pd(dien)X]^+$ could not be studied in detail kinetically, the sterically hindered systems $[Pd(Et_4\text{-}dien)X]^+$ (X = Cl, Br) were allowed to react with a series of nucleophiles, and rate constants were determined. As shown in Figure 2, the rates of reaction with reagents such as Br^-, I^-, SCN^-, N_3^-, and NO_2^- are completely independent of the reagent concentration in the 0.005 to 0.1 *M* range. In several runs the ionic strength was held constant by the addition of an inert electrolyte and variations in rate were not observed, beyond an experimental error in measurement of *ca.* 5-10%. The only reagent which behaved differently was hydroxide ion, and a dependence of the rate on this reagent was observed consistent with rate law

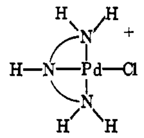
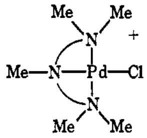
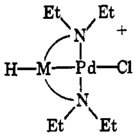
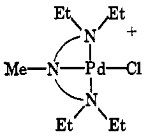
$$k_{obsd} = k_1 + k_2[OH] \tag{10}$$

The extrapolated intercept for the hydroxide ion reaction is the same value as the first-order rate constants for the reactions of all the other nucleophiles with the substrate. This behavior for these Pd(II) complexes is diametrically opposed to the usual reagent reactivity for square-planar complexes where it is found that OH^- is a poor reagent and others, particularly I^- and SCN^-, are excellent nucleophiles. The gross kinetic behavior is quite similar to that observed for octahedral cobalt(III) complexes,[22] where it is held that bond breaking is of major importance in the kinetic act. Because of this similarity in *kinetic* behavior, these sterically hindered square-planar complexes were referred to as pseudo-octahedral complexes.[4a]

Considering the compounds shown in Table VIII, there is an interesting similarity shown by a comparison of the rate of the reaction of compound III with that of IV and the rates of reaction of a series of analogous Co(III) complexes containing a varying number of N-H bonds.[23] For example, the relative rates of aquation at 25° of *cis*-$[Co(en)_2Cl_2]^+$ and *cis*-$[Co(trien)Cl_2]^+$ (en = ethylenediamine, $H_2NCH_2CH_2NH_2$; trien = triethylenetetramine, $H_2NC_2H_4NHC_2H_4NHC_2H_4NH_2$) are 1.7 and 1, respectively; the relative rates of aquation of *trans*-$[Co(en)(NH_3)_2Cl_2]^+$ and *trans*-$[Co(en)_2Cl_2]^+$ are 7 and 1, respectively. The rates of reaction in these systems increase with increasing numbers of N-H bonds, and this was attributed in part to an increase in energy of solvation. An increase in rate is also found in going from complex IV with no N-H bonds to III with one such bond. However, this effect may be dominated by other effects in the reactions of these pseudo-octahedral complexes. For example, the rate of reaction of complex II with no N-H bonds is 130 times larger than that of complex III with one N-H bond.

It is also of interest to note that for N-monoalkylethylenediamine complexes of the type *trans*-$[Co(AA)_2Cl_2]^+$, the rates of reaction increase with an increase in size of the alkyl group.[24] Thus the relative rates of aquation at 25° of the above cobalt(III) complexes, where AA = $CH_3NHC_2H_4NH_2$ and *n*-$C_3H_7NHC_2H_4NH_2$, are 1 and 7, respectively. This is a markedly different behavior from that of the reaction of the ethyl derivative (IV) compared with the methyl derivative (II). In these systems there is an increase in rate with a decrease in size of the alkyl group.

Table VIII. Reactivity of Some Pd(II) Substrates as a Function of Number of N-Alkyl Groups[a]

	Substrate	k, sec^{-1}	Rate rel to MeEt$_4$dien complex
I		100	100,000
II		0.3	400
III		0.002	3
IV		0.0008	1

[a] The actual rate of hydrolysis was not measured. However, as will be discussed later, since the Et$_4$dien, Me$_5$dien, and MeEt$_4$dien complexes react with all reagents (except hydroxide in the case of Et$_4$dien) at a rate which is reagent independent, it is assumed that the rate-determining step is the reaction of the complex with the solvent water. In the case of the unhindered $[Pd(dien)Cl]^+$, the value of k_{obsd} has been estimated, since it was slightly too fast to measure, with the stopped-slow apparatus and refers to the reaction of OH^- with $[Pd(dien)Cl]^+$. For this reaction it is believed that the rate-determining step is the reaction of the solvent water with the substrate, followed by a proton transfer in the basic solution to give the product, $[Pd(dien)OH]^+$.

The explanation given[24] for steric acceleration in the Co(III) complexes is that usually given for a dissociative process, *i.e.*, steric crowding in the ground state enhances the formation of a lower coordinated transition state. In contrast to Co(III) behavior, a decrease in rate is found in going from II to IV, and this fact suggests that the steric acceleration effect found for the octahedral complexes of Co(III) is not making as important a contribution to the rates of reaction of these pseudo-octahedral systems. An examination of molecular models shows that this is reasonable, because there is considerable strain in the six-coordinated Co(III) complexes containing bulky ligands, but no appreciable strain in the four-coordinated Pd(II) complexes. In fact, there is experimental evidence that Ni(II), which is smaller than Pd(II), forms stable five-coordinated complexes with Me$_5$dien and Et$_4$dien.[5]

That complex II reacts 400 times faster than does IV, and that both react at rates independent of the entering

---

[22] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

[23] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Chem. Phys.*, **59**, 304 (1955).

[24] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Am. Chem. Soc.*, **75**, 3089 (1953).

reagent, is indicative of greater solvent assistance in the reactions of II compared to IV if one assumes that a solvent-assisted dissociative process is operative. Alternatively, these same results are explicable in terms of a bimolecular solvolysis since the less-hindered complex (II) reacts much faster than the more-hindered complex (IV). In reactions of some Co(III) systems in aqueous solution, it is held that the most important contribution to the energetics is the stretching of the Co–X bond, a process which is assisted by the solvent.[25] These systems do not have much discriminating ability for various reagents, and therefore water which is always present in much larger concentrations than other reagents will assume the role of the nucleophile.

It seems that this same explanation is valid for the reactions of the pseudo-octahedral complexes II, III, and IV. The least sterically hindered complex (II) gets the greatest assistance from the solvent water in its reactions and as a result is the fastest to react. Complex II, in all reactions studied, showed no tendency toward second-order kinetics, even though ample space exists above and below the square plane for higher coordinated species to form. It is therefore suggested that a solvent-assisted dissociative process is operative in these pseudo-octahedral complexes, and that the reactions proceed as shown by eq 11 and 12. In support of this reaction scheme is the fact that the rate of reaction 12 is "instantaneous" for $Y^- = OH^-$ and fast for other reagents Y^-, but the rates of formation of $[\mathrm{Pd(R_5dien)Y}]^+$ are identical for $Y^- = OH^-$ and for all other reagents studied. The only exception to this is complex III which contains an N–H bond, and its special behavior in basic solution is explained below.

$$[\mathrm{Pd(R_5dien)Cl}]^+ + \mathrm{H_2O} \xrightarrow{\text{slow}} [\mathrm{Pd(R_5dien)H_2O}]^{2+} + \mathrm{Cl^-} \qquad (11)$$

$$[\mathrm{Pd(R_5dien)H_2O}]^{2+} + \mathrm{Y^-} \xrightarrow{\text{fast}} [\mathrm{Pd(R_5dien)Y}]^+ + \mathrm{H_2O} \qquad (12)$$

The reaction of hydroxide ion with the $\mathrm{Et_4dien}$ complexes proceeds by a two-path mechanism. The first-order path related to k_1 in (10) is believed to be the same as that described above for the other reagents. That is to say, as shown in Figure 2, extrapolation of the hydroxide rate to zero hydroxide ion concentration gives an intercept which is the same as the rates of other nucleophiles, thus indicating a common reaction intermediate. Conspicuously different from the other reagents, however, is the dependence on hydroxide ion concentration, which is related to k_2 in (10). Two mechanisms would ostensibly explain this base catalysis. First of all, since hydroxide ion is smaller in size than any of the other reagents studied, it may be that this ion could displace the acido group by an S_N2 process. A second, and we think more plausible, mechanism could be that of a rapid acid–base equilibrium followed by a reaction of the conjugate base. A large body of experimental evidence concerning the base catalysis of Co(III) solvolytic reactions has been explained in terms of a conjugate-base mechanism.[22] By virtue of the fact that metal ammines are weak acids, although considerably weaker than metal aquo complexes, a proton may be lost from one of the amine nitrogen atoms in strongly basic solution to form an amido complex. An obvious prerequisite for a reaction of this type is that the amine nitrogen atoms have a hydrogen atom attached Such is the case for $\mathrm{Et_4dien}$, since it has a hydrogen atom on the central nitrogen atom. Complexes such as those of $\mathrm{Me_5dien}$ and $\mathrm{MeEt_4dien}$ do not have N-hydrogen atoms, so a comparison of the reaction of hydroxide ion with $\mathrm{Et_4dien}$ and $\mathrm{MeEt_4dien}$ complexes should differentiate between the two mechanisms.

The cation $[\mathrm{Pd(MeEt_4dien)Cl}^+$ reacts with hydroxide ion over the range from 0.01 to 0.1 *M* at a rate which is independent of the hydroxide ion concentration. Also, $[\mathrm{Pd(Me_5dien)Cl}]^+$ shows a similar behavior, and these results are then good evidence for a conjugate-base mechanism in the $[\mathrm{Pd(Et_4dien)X}]^+$ system. Such a mechanism has never been invoked for d^8 square-planar complexes since, with the exception of Banerjea and Tripathi's work, the conclusions of which are debatable, no base catalysis had been observed in these systems.[26]

The base hydrolysis of $[\mathrm{Pd(Et_4dien)X}]^+$ complexes may be formulated as in eq 13–17. The rate for such a scheme is expressed by eq 18, where $K_{eq} = K_a/K_w$ (K_a is the acid dissociation constant of $[\mathrm{Pd(Et_4dien)X}]^+$). It one assumes that K_a is approximately equal to K_w, a value of 0.055 $\sec^{-1}$ for k_{CB} is obtained from the data plotted in Figure 2. Since $k_{\mathrm{H_2O}}$ is 0.002 $\sec^{-1}$, base hydrolysis exceeds acid hydrolysis by a factor of about 30. This ratio is similar to the value of 60 found for the ratio of the rates of reaction of $[\mathrm{Au(Et_4dien{-}H)Cl}]^+$ and $[\mathrm{Au(Et_4dien)Cl}]^{2+}$.[3b]

$$[\mathrm{Pd(Et_4dien)X}]^+ + \mathrm{H_2O} \xrightarrow[\text{slow}]{k_{\mathrm{H_2O}}} [\mathrm{Pd(Et_4dien)H_2O}]^{2+} + \mathrm{Cl^-} \qquad (13)$$

$$[\mathrm{Pd(Et_4dien)H_2O}]^{2+} + \mathrm{OH^-} \xrightarrow[\text{fast}]{\text{very}} [\mathrm{Pd(Et_4dien)OH}]^+ + \mathrm{H_2O} \qquad (14)$$

$$[\mathrm{Pd(Et_4dien)X}]^+ + \mathrm{OH^-} \xrightleftharpoons{K_{eq}} [\mathrm{Pd(Et_4dien{-}H)X}] + \mathrm{H_2O} \qquad (15)$$

$$[\mathrm{Pd(Et_4dien{-}H)X}] \xrightarrow[\text{slow}]{k_{CB}} [\mathrm{Pd(Et_4dien{-}H)}]^+ + \mathrm{X^-} \qquad (16)$$

$$[\mathrm{Pd(Et_4dien{-}H)}]^+ \ \mathrm{H_2O} \xrightarrow{\text{fast}} [\mathrm{Pd(Et_4dien)OH}]^+ \qquad (17)$$

$$\text{rate} = k_{\mathrm{H_2O}}[\text{complex}] + k_{CB}K_{eq}[\text{complex}][\mathrm{OH}] \qquad (18)$$

In summarizing the kinetic behavior of these sterically hindered Pd(II) complexes, it seems appropriate to say that a solvent-assisted dissociation takes place. The steric retardation observed suggests that the nucleophile water is involved in the rate-determining step. However, the fact that all reagents studied, except hydroxide ion, failed to react directly with the complex indicates that considerable stretching of the Pd–X bond has occurred in the transition state. This point is particularly evident with $[\mathrm{Pd(Me_5dien)X}],^+$ because molecular models show that some vacant space exists above and below the plane for entry of a nucleophile. Finally, the base catalysis which most probably is due to a conjugate-base mechanism corroborates the idea that bond breaking is important, since the lower-charged amido complex reacts about 30 times faster than the parent acid.

Acknowledgment. This research was supported by U. S. Atomic Energy Commission Grant COO-1087-99.

---

[25] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, 3, 1336 (1964).

[26] Investigation of anchimeric effects in reactions of Pt(II) complexes show that the reaction of *trans*-$[\mathrm{Pt(H_2NC_2H_4OH)_2Cl_2}]$ depends on the concentration of OH: K. H. Stephen and F. Basolo, *Inorg. Nucl. Chem. Letters*, 2, 23 (1966).