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Kinetics of Ammonation of *Trans*-Dichlorobis(triethylphosphine)platinum(II), *Trans*-Dichloro(triethylphosphine)ammineplatinum(II), and *Trans*-Dichlorodiammineplatinum(II)[1]

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A conductivity method was utilized to study the kinetics of the successive replacement of chloride ligands by ammonia in methanol solvent for the three complexes. For t–$Pt(P(C_2H_5)_3)_2Cl_2$ *there was an induction period and complete description of the kinetics was not achieved. The second ammonation step for this compound was not complete but approached an equilibrium steady state. For* t–$Pt(NH_3)_2Cl_2$*, solvation and ammonation occurred at comparable rates. For* t–$Pt(P(C_2H_5)_3)_2Cl_2$ *each ammonation proceeded essentially to completion by a second order process. At 35°C it appeared that the ammonation rates of all three complexes did not differ greatly so little* cis *effect was apparent. In each case the second ammonation rate constant was an order of magnitude lower than that for the initial ammonation reaction.*

Introduction

A kinetic *trans* effect upon the ligand substitution reactions for platinum(II) complexes is well recognized and various theories have been presented to account for it.[2] However, it has been shown that for the weakly trans-directing ligands of NH_3 and Cl^-, a *cis*-effect apparently plays as significant a role as the *trans*-effect.[3] The present work was undertaken to compare the *cis*-effects between a strongly *trans*-directing phosphine and the weakly *trans*-directing ammonia group. The three complexes, *t*–$Pt(P(C_2H_5)_3)_2Cl_2$, *t*–$Pt(NH_3)(P(C_2H_5)_3)Cl_2$ and *t*–$Pt(NH_3)_2Cl_2$, all have the same (zero) charge, and for each there is a chloride *trans* to the chloride which is replaced initially. The principal difference between the complexes resides in the nature of *cis* neighbors. For chloride and bromide exchange and replacement reactions, Carturan and Martin found little difference in the *cis*-effect of triethylphosphine, ammonia and diethylbenzylamine.[4] However, one consequence of this work was the demonstration that the reactions of *trans*-dichlorobis(triethylphosphine)platinum(II) were unexpectedly slow in comparison to those of related complexes. The present work provides some further information about anomalous behavior of this compound.

Experimental Section

Experiments were performed at 25.0° and 35.0° so a close comparison of the ammonation with the chloride and bromide displacement reactions could be obtained. Also, the same solvent, methanol, was employed which provides a suitable solubility for the phosphine complexes. However, the solubility of *t*–$Pt(NH_3)_2Cl_2$ was so low that kinetics experiments were attempted only for 35.0°.

Since replacement of chloride by NH_3 from a neutral complex yields a pair of ions, a conductimetric technique was utilized. From reasonable values for ionic mobilities the conductances provide an estimate of the absolute extent of reaction which cannot be obtained spectrophotometrically without isolation of products and intermediates.

Materials. A platinum stock had been purified by the technique of Jowanovitz *et al.*[5] to reduce the iridium content to the level of 0.020 ppm. Preparation of K_2PtCl_6, K_2PtCl_4, $[Pt(NH_3)_4]Cl_2$ and *t*–$Pt(NH_3)_2Cl_2$ followed procedures described in previous work.[6]

Trans-Dichlorobis(triethylphosphine)platinum(II). This complex was prepared by either the reaction between $P(C_2H_5)_3$ and K_2PtCl_6 or the reaction of $P(C_2H_5)_3$ with K_2PtCl_4 according to the procedures of Jensen.[7]

The product from either of these preparations was extracted into boiling ether in which the *cis*-complex is insoluble. The extraction was under a bright light to effect the isomerization of the *cis*- to the *trans*-compound. Bright yellow crystals were obtained which were recrystallized from methanol under weak red light until no changes in the ultraviolet spectrum were discerned. The melting range of the crystals was 142-142.3°C.

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(1) Work was performed at the Ames Laboratory of the U.S. Atomic Energy Commission.

(2) a) Basolo F. and Pearson R.G., « Mechanism of Inorganic Reactions », (2nd Ed., Wiley, New York, 1967) Chapt. 5.
b) Basolo F., « Progress in Inorganic Chemistry », Cotton F.A., (Wiley, Interscience, New York, 1962) Vol. 4.
c) Langford C.H. and Gray H.B., « Ligand Substitution Processes », (Benjamin, New York, 1965) Chapt. 2.

(3) Martin, Jr., D.S., *Inorg. Chim. Acta Reviews, 1,* 87 (1967).

(4) Carturan G. and Martin, Jr., D.S., *Inorg. Chem.*, *9*, 258 (1970).

(5) Jowanovitz L.S., McNatt F.M., McCarley R.E., and Martin, Jr., D.S., *Anal. Chem.*, 32, 1270 (1960).

(6) (a) Martin Jr., D.S. and Adams R.A., « Advances in Chemistry of the Coordination Compounds », McMillan Co., New York, 1961, p. 579.
(b) Grantham L.F., Elleman T.S., and Martin, Jr., D.S., *J. Am. Chem. Soc.*, 77, 2965 (1955).

(7) Jensen K.A., *Z. Anorg. Chem.*, *229*, 252 (1936).

Trans-Dichloroammine(triethylphosphine)platinum-(II). The chloro bridged dimer complex, *sym-trans*-di-μ-chloro-dichlorobis(triethylphosphine)diplatinum-(II) was prepared by the method described by Chatt.[8] The product was extracted and recrystallized several times from acetone, and then from methanol. Because a band in the ultraviolet spectrum at 272 nm coincides with an absorption of acetone there was some concern that this product was contaminated by acetone. However, a fast neutron activation analysis for oxygen indicated only 790 ppm; and from this level it could be concluded that absorption by acetone in this region was not significant. To convert the dimer, $[PtCl_2(P(C_2H_5)_3)]_2$, into $t\text{–}Pt(P(C_2H_5)_3)(NH_3)Cl_2$, the stoichiometric amount of standardized solution of NH_3 in anhydrous ethanol was added to its ethanol solution. Following evaporation of the ethanol, the yellow crystals were recrystallized from petroleum ether, boiling range 80-100°C. The infrared spectrum showed the single ν(Pt–Cl) band at 339.5 cm^{-1} expected for the *trans*-isomer.

In a mass spectrum the ions of the parent compound were identified. However, the most intense mass peaks corresponded to 17 mass units less than the parent compound, indicating that in the ion source NH_3 was readily lost. A melting point for the compound could not be obtained. Sublimation would begin at 110°C but as the temperature was raised to 130° the residue changed from pale yellow to orange yellow. Ultraviolet spectra revealed that while sublimate was the $t\text{–}Pt(P(C_2H_5)_3)(NH_3)Cl_2$ the residue was the dimer, $[Pt(P(C_2H_5)_3)_2Cl_2]_2$.

Reaction Solutions. A spectrochemical grade of methanol was used to prepare the reaction solutions. Its specific conductance was found to be 1.0×10^{-6} $ohms^{-1}$ cm^{-1}. All the reactions were studied in a solution of 0.01 *M* KCl in the methanol. The KCl served to suppress the solvolysis of the complex, to establish a nearly constant ionic strength, and to bring the resistance of the solutions in the cells into the convenient 1000-10,000 ohm region for measurement. The ammonia solutions were prepared by passing anhydrous NH_3 through the methanol. The concentration of NH_3 was determined by titration with a standard sulfamic acid solution with a methyl red end-point.

Conductance Measurements. The conductivity cells had bright platinum electrodes and were designed to conform to the recommendations of Jones and Bollinger[9] and had cell constants of about 6.4 cm^{-1}, from calibrations with 0.02 *M* *a*queous KCl. The cells were immersed in a thermostat utilizing a transformer oil bath which was maintained to within ±0.02°C of the set-point. The conductivity for a 1.00 khz current was measured by means of a General Radio Co. Type 71C capacitance bridge with the output from the bridge determined by a Tetronix Type 122 preamplifier, and a General Radio Type 1231B amplifier and null-detector. The oscillator voltage was only applied during the measurement of resistances.

The signal generator and thermostat were in a darkened room with only dim red lights and located 12 meters from the capacitance bridge. It was found that when any solution was introduced into the cells, the resistance initially dropped rapidly, apparently from evaporative cooling. Solutions stabilized within 15 minutes. However, it was not possible to measure «zero time» resistances because of this effect.

To start an experiment, a solution of NH_3 in the 0.01 *M* KCl was added to a solution of the complex in 0.01 *M* KCl. This time of mixing was recorded as zero time. The solution was added to the conductivity cell. Measurements of the resistance were performed repeatedly and 100 or more values would be recorded over a period of several days. It was noted that the resistance continued to decrease slowly after the substitution reaction was substantially completed. A similar drop of resistance was noted in solutions containing only NH_3 in methanolic KCl so it was concluded that there was a very slow leaching of ions from the glass walls of the cells. An «infinity-time» conductance therefore could not be measured. However, the conductances of the solution were followed for a sufficiently long time that this slow rise in conductance could be extrapolated to zero time with reasonable confidence. This extrapolated resistance has been designated R_∞ which is a function of time. The conductances, 1/R(t) measured during the course of the reaction were subtracted from the coresponding $1/R_\infty$ to provide the changes caused by the course of the ammonation reactions.

Results and Discussion

In the ammonation of the *trans*-dichloro complexes the possible reversible reactions can in each case be written

$$t\text{–}PtL_2Cl_2 + NH_3 \leftrightarrows t\text{–}PtL_2(NH_3)Cl^+ + Cl^- \qquad (1)$$

and

$$t\text{–}PtL_2(NH_3)Cl^+ + NH_3 \leftrightarrows t\text{–}PtL_2(NH_3)Cl_2^{2+} + Cl^-, \qquad (2)$$

where the L represents the non-replaced neutral ligands in the starting complex, either triethylphosphine or ammonia.

The conductance is expected to be described by the equation,

$$1/R(t) = 1/R(0) + \frac{1}{1000\,k}(\Lambda_{[PtL_2(NH_3)Cl]Cl}[PtL_2(NH_3)Cl^+] + 2\Lambda_{[PtL_2(NH_3)_2]Cl_2}[PtL_2(NH_3)_2^{2+}]) \qquad (3)$$

where the Λ's are equivalent conductances of the salts in question, the brackets represent molar concentrations, and k is the cell constant. 1/R(0) contains the contribution from the KCl in the solution; and since $[Cl^-]$ and ionic strength are substantially unchanged, the equivalent conductances of the two products are expected to remain substantially constant. Some contribution to the conductance also resulted from the acid-base equilibrium between NH_3 and the solvent.

The formation of ion pairs, which can be expected to be greater in a non-aqueous solvent than in water, will reduce the equivalent conductance of a salt.

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[8] Chatt J., *J. Chem. Soc.*, 652 (1951).
[9] Jones S. and Bollinger G.M., *J. Am. Chem. Soc.*, 53, 411 (1931).

There is not a unanimity concerning the extent of ion pair formation for even a simple electrolyte as KCl. Various workers have estimated that the association or ion pair formation constant for their electrolytes, defined in equation (4), ammounts to 1.2 to 14.7 M^{-1} at 25°C

$$[p]+[n]\rightarrow[p{-}n];\ K=\frac{[p{-}n]}{[p][n]} \tag{4}$$

where [p] refers to the positive ion, [n] refers to the negative ion and [p–n] refers to the ion pair. However, when ionic atmosphere and anion concentration was maintained essentially constant in a series of experiments the fractional ion pair formation is expected to remain constant.

Each of the complexes studied exhibited substantially different behavior in these studies, hence the results for each one will be discussed separately.

Trans–$[Pt(P(C_2H_5)_3(NH_3)Cl_2]$. Of the three compounds under study the kinetics of this compound were the best characterized. It was apparent from the conductance *vs.* time curves that reactions (1) and (2) for this system proceded to completion in the presence of excess NH_3. Plots of $1/R_\infty - 1/R(t)$ gave two periods from which initial values of pseudo first order rate constants could be estimated. Since the replacement of the first chloride was approximately 10 times faster than that for the second chloride the periods were readly resolved. A final refinement of the rate constants was obtained in the following way. With each of reactions (1) and (2) considered as possibly reversible reactions the differential equations to describe the kinetcs were taken to be:

$$\begin{aligned}\frac{d[PtL_2(NH_3)Cl^+]}{dt} &= +k_{1-NH_3}[NH_3][PtL_2Cl_2]\\ &-(k_{-1}[Cl^-]+k_{2-NH_3}[NH_3])[PtL_2(NH_3)Cl^+]\\ &+k_{-2}[Cl^-][PtL_2(NH_3)_2^{2+}],\end{aligned} \tag{5}$$

and

$$\begin{aligned}\frac{d[PtL_2(NH_3)_2^{2+}]}{dt} &= k_{2-NH_3}[NH_2][PtL_2(NH_3)Cl^+]\\ &-k_{-2}[Cl^-][PtL_2(NH_3)_2^{2+}].\end{aligned} \tag{6}$$

The additional constraints were:

$$[NH_3]=[NH_3]_0-[PtL_2(NH_3)Cl^+]-2[PtL_2(NH_3)_2^{2+}], \tag{7}$$

and

$$[Cl^-]=[Cl]_0+[PtL_2(NH_3)Cl^+]+2[PtL_2(NH_3)^{2+}]. \tag{8}$$

From the initial concentration and a set of rate constants the concentration of each species could be calculated by a Runge-Kutta technique[10] with the IBM 350-65 computer of the Iowa State Computer Center. From the concentration of each species the conductance of a solution $(1/R - 1/R_o)$ could be calculated for comparison with experimental measurements from equation(3) with the two additional parameters, $\Lambda_{[PtL_2(NH_3)Cl]Cl}$, $\Lambda_{[PtL_2(NH_3)_2]Cl_2}$ and $1/R(0)$. With k_{-1} and k_{-2} set equal to zero, a set of Λ, s and k, s was sought which would reproduce the experimental data. The conditions of the experiments are given in Table I. A set of values for k_1,k_2 and for $\Lambda_{[PtL_2(NH_3)Cl]Cl}$ was found which described the experimental conductances satisfactorily with 0.01M initial chloride if a small dependence of $\Lambda_{[PtL_2(NH_3)_2]Cl_2}$ upon the initial complex concentration was permitted. Values of the parameters are also in Table I. Although only a subjective test of the calculation was made, it was rather severe since generally all experimental values of $1/R_\infty - /R(t)$ fell within 2% of the calculated curves.

The relatively high values for $\Lambda_{[Pt(P(C_2H_5)_3)(NH_3)_2Cl]Cl}$ which were constants in experiments at 0.01*M* KCl in methanol indicates that ion pair formation was not an important factor for the +1 ion of this salt. In addition, the equivalent conductance for this salt changed by nearly the same factor as that for the KCl solution between the ionic strengths 0.01 and 0.03*M*. On the other hand both the lower values for $\Lambda_{[Pt(P(C_2H_5)_3)(NH_3)_3]Cl_2}$ and the dependence upon complex concentration indicates a greater, but not overwhelming ion pair formation by the +2 ion and chloride.

The experiment in which H_2O was added to the solvent was especially gratifying since it indicated that the rate constants were not changed significantly by this fairly massive addition of H_2O. Therefore, it is unlikely that traces of H_2O which might have been absorbed from the atmosphere influenced the rate constants to a significant degree. There was an increase in Λ for $[t\text{-}Pt(P(C_2H_5)_3)(NH_3)_3]Cl_2$ upon the addition of H_2O whereas the value for $[t\text{-}Pt(P(C_2H_5)_3)(NH_3)_2Cl]Cl$ was not changed. This result supports the above conclusion concerning the magnitude of ion pair formation since the presence of H_2O should enhance the solvation of ions and the dissociation of ion pairs. The relative constancy of the Λ's over rather wide variations of NH_3 concentration indicates that both ammonations were substantially complete.

The activation enthalpies for ammonation are rather normal for ligand substitution reactions of platinum(II) complexes as are the moderately large negative activation entropies. It is noted that the ammonation rate, in even the slowest reaction was at least 4 times faster than the solvation rate which was indicated from isotopic exchange reactions.[4]

Trans–$Pt(NH_3)_2Cl_2$. This complex was not extensively studied. For one thing, a twelve hour equilibration of methanol with the compound at 35°C produced a solution of only 0.146 m*M* which was near the limit of its solubility. At such low concentration, noise was a serious problem, and experiments were not attempted at 25° where the solubility and equivalent conductances were even lower. The technique used to analyze the data for t–$Pt(P(C_2H_5)_3)(NH_3)Cl_2$ could not be used since equation (5) did not properly describe the kinetics.

The semilogarithmic plot of $[1/R_\infty - 1/R(T)]$ *vs.* time was resolved into two components of nearly equal conductance change. Since NH_3 was present in large excess, pseudo first-order conditions applied. The pseudo first order constants k_1' and k_2' were calculated from $(\ln 2)/\tau_{1/2}$ of the rapid and slow components respectively. The experimental conditions are given in Table II together with the indicated pseudo rate constants k_1' and k_2'.

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(10) Scarborough J.B., « Numerical Mathematical Analysis », 4th Ed. John Hopkins Press, Baltimore, Md., 1958, p. 314.

Table I. Ammonation of *t*–$[Pt(PEt_3)(NH_3)Cl_2]$ in 0.010*M* KCl.

$[Pt(PEt_3)(NH_3)Cl_2]_0$ m*M*	$[NH_3]_0$ m*M*	$\Lambda_{[PtL_2(NH_3)Cl]Cl}$ $cm^2ohm^{-1}N^{-1}$	$\Lambda_{[PtL_2(NH_3)_2]Cl_2}$ $cm^2ohm^{-1}N^{-1}$
	25°C $k_{1-NH_3}=5.4\times10^{-4}$,	$k_{2-NH_3}=4.9\times10^{-5}M^{-1}sec^{-1}$	
0.277	1310	59.1	48.2
0.480	»	»	47.8
0.592	989	»	47.4
0.601	600	»	»
0.803	1240	»	47.1
	35° $k_{1-NH_3}=14.2\times10^{-4}$,	$k_{2-NH_3}=12\times10^{-5}M^{-1}sec^{-1}$	
0.241	100	67.9	55.4
0.649	89.9	»	52.7
»	41	»	»
0.650	173	»	»
0.787	604	»	»
0.951	100	»	51.0
0.622 [a]	320	56.3	41.3
0.657 [b]	352	67.9	55.8

$\Delta H_1^*=17\pm1$. $\Delta H_2^*=16\pm2$ kcal/mole

$\Delta S_1^*=-17\pm3$. $\Delta S_2^*=-26\pm5$ cal/deg mole

[a] In this experiment the KCl was 0.03 *M* KCl. [b] In this experiment H_2O was added to 2% by volume.

Table II. Ammonation of *t*–$[Pt(NH_3)_2Cl_2]$ at 35°C.

$[Pt(NH_3)_2Cl_2]_0$ m*M*	$[NH_3]_0$ m*M*	$[KCl]_0$ m*M*	$10^5\times k_1$ [a] sec^{-1}	$10^5\times k_2$ [b] sec^{-1}
0.135	166	10	34.0	3.11[b]
0.139	168	10	30.4	3.45
0.135	463	10	62.5	9.17
0.146	496	10	66.8	10.8
0.134	589	10	82.5	10.9

[a] From the least-squares fit of these values to the equation, $k'=k_{1-NH_3}[NH_3]+k_s$; $k_{1-NH_3}=1.13\pm0.08\times10^{-3}M^{-1}sec^{-1}$, $k_s=1.3\pm0.3\times10^{-4}sec^{-1}$. [b] From the least-squares fit of these values to the equation, $k_2'=k_{2-NH_3}[NH_3]$, $k_{2-NH_3}=1.98\pm0.07\text{-}\times10^{-4}M^{-1}sec^{-1}$.

It is apparent from the data that k_1' can not be represented by the expression, $k_{1-NH_3}[NH_3]$ but rather is fitted by

$$k_1'=k_s+k_{1-NH_3}[NH_3] \qquad (9)$$

An expression of the form of equation 9 is frequently found for platinum(II) complexes when the solvent competes with the attacking nucleophile as in the reaction

$$t\text{–}Pt(NH_3)_2Cl_2+CH_3OH\xrightarrow[k_s]{}t\text{–}Pt(NH_3)_2Cl(CH_3OH)^++Cl^-. \qquad (10)$$

Following the solvation the entering nucleophile usually replaces the solvent rapidly. It appears more likely that in this case, however, from the analogy of the methanol solvent to H_2O, that the NH_3 removes a proton from the methanol ligand to give the product:

$$t\text{–}Pt(NH_3)_2Cl(CH_3OH)^++NH_3 \rightarrow t\text{–}Pt(NH_3)_2Cl(CH_3O)+NH_4^+. \qquad (11)$$

In any event, a pair of ions are produced by the solvation in competition with the formation of *t*–$Pt(NH_3)_3Cl^+$. The results of a least squares evaluation of k_s and k_{1-NH_3} are given in Table II.

In the slowest reaction the solvation reaction was about · 6 of $k_{1-NH_3}[NH_3]$. It was found that k_2' was well represented by $k_{2-NH_3}[NH_3]$ and a least squares value of 1.98×10^{-4} sec^{-1} M^{-1} was indicated. Note that this was not the rate constant for a pure complex species, since presumably both $Pt(NH_3)_3Cl^+$ and $Pt(NH_3)_2Cl(CH_3O)^+$ were undergoing ammonation.

Trans-Dichlorobis(triethylphosphine)platinum(II). The kinetics for ammonation of this compound proved to be unexpectedly complex and a complete characterization of these kinetics has not been attained.

First of all, the rate of increase of conductance was somewhat slower than for the other two complexes upon the addition of NH_3. However, this rate slowly increased until it had approximately doubled. This increase in the rate of change of conductance was reproducible under a given set of conditions. No difference was observed between a freshly prepared solution of the complex and a solution which had been prepared 12 to 24 hours earlier. The time from the start of an experiment to the inflection point in the rate curve will be designated as the induction period for the reaction.

Secondly, following a change of conductance corresponding to the stoichiometric replacement of one Cl^- ligand by NH_3 there was a continued increase in conductivity at a much slower rate. However, this second increase in conductivity corresponded to the replacement of considerably less than 1 Cl^- ligand per Pt-complex. It appears therefore that the second ammonation, instead of proceeding essentially to completion, approached an equilibrium steady state. Therefore the kinetics must be treated as a reversible process.

The above features of the ammonation reactions were also confirmed qualitatively by spectrophotometric means. The spectrum of a reacting solution was scanned repeatedly by a Cary Model 14 spectrophotometer from 400 to 200 nm during the course of an ammonation reaction. The spectrum of the t–$Pt(P(C_2H_5)_3)_2Cl_2$ in methanol is dominated by a pair of peaks, one at 247.5 nm, $\varepsilon = 1.06 \times 10^4$ cm^{-1} M^{-1} and a second at 267 nm, $\varepsilon = 1.02 \times 10^4$ cm^{-1} M^{-1}. During the early reaction periods these two peaks diminished in size as the t–$Pt(P(C_2H_5)_3)_2Cl_2$ disappeared and a peak at 233 nm appeared. The height of this new peak passed through a maximum, but even at very long times it did not disappear. It apparently can be attributed to the t–$Pt(P(C_2H_5)_3)_2(NH_3)Cl$ which remained at an appreciable equilibrium concentration. When the absorbance of the peak at 267 nm was plotted as a function of time, an increase in the rate of disappearance of this peak was clearly apparent, confirming the induction period observed conductimetrically.

A number of experiments were performed to investigate the induction period for the reaction. A solution was allowed to react to the final steady state. A small quantity of his final equilibrium solution was added to a freshly prepared kinetics mixture. The addition corresponded to 3.7 per cent of the fresh solution. The initial reaction rate was much greater and there was no inflection in the conductance curve. Thees results are shown in Figure 1. Small amounts of possible impurities were added in other experiments. Both c–$Pt(P(C_2H_5)_3)_2Cl_2$ and t–$Pt(P(C_2H_5)_3)_2(H)Cl$ reacted very rapidly with NH_3 because of the strong *trans*-directing properties of hydride and triethylphosphine ligands. The change in conductivities following the fast reactions of these adducts are also shown in Figure 1. It can be seen from the curves that whereas the addition c–$Pt(P(C_2H_5)_3)_2Cl_2$ had no effect, both t–$Pt(P(C_2H_5)_3)_2(H)Cl$ and t–$Pt(P(C_2H_5)_3)_2Cl_4$ extended the induction period.

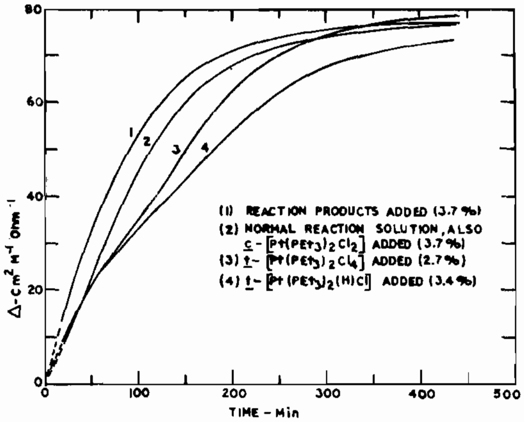

Figure 1. Influence of four added compounds on the molar conductances during the ammonation of t–$Pt(P(C_2H_5)_3)_2Cl_2$ at 35°. For the solution without additions, $KCl = 0.01M$, $[Pt]_0 = 0.644mM$, and $[NH_3]_0 = 0.18M$. In other experiments the $[Pt]_0$ concentrations were in the range of 0.608–$0.651mM$ and $[NH_3]_0$ in the range of 0.199–$0.217M$.

The induction period may result from an autocatalytic process in which one of the products of the ammonation reaction serves as a catalyst to accelerate the ammonation of t–$Pt(P(C_2H_5)_3)_2Cl_2$. If so, the initial rate of the reaction, before the formation of products, will characterize the uncatalyzed reaction.

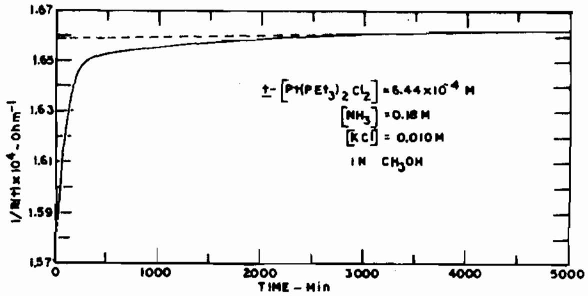

Figure 2. Conductance *vs* time in an ammonation experiment for t–$Pt(P(C_2H_5)_3)_2Cl_2$ at 35°.

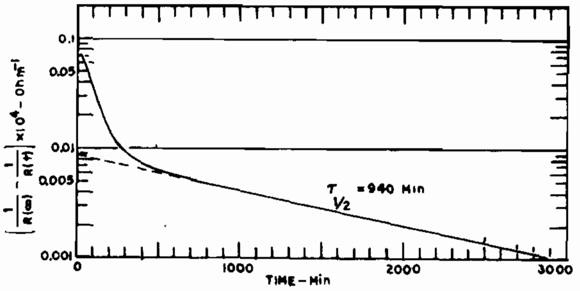

Figure 3. Semilogarithmic plot of $[1/R_\infty - 1/R(t)]$ for the experiment in Figure 2.

Results of one of the kinetics experiments is illustrated in Figures 2 and 3 which will illustrate the treatment of the data. In Figure 2, $1/R(t)$ has been plotted. The dashed line is the linear extrapolation of the conductance, $1/R_\infty$, resulting from the slow leaching of the glass cell. In Figure 3 is presented plot of $\log\ [1/R_\infty - 1/R(t)]$ *vs.* time. The component with the 940 min half-life apparently describes the pseudo first order approach to the equilibrium with respect to the second ammonation process in accordance with the equation,

$$\frac{d[PtL_2(NH_3)_2]}{dt} = k_2' \, [PtL_2(NH_3)Cl^+] - k'_{-2} \, [PtL_2(NH_3)_2^{2+}]. \quad (12)$$

The straight line portion of the plot in Figure 3 describes the change in conductivity following the completion of the first ammonation. For this linear portion, the value of $[1/R_\infty - 1/R(t)]_2$ will be:

$$[1/R_\infty - 1/R(t)]_2 = \frac{1}{1000\ k}(2\Lambda_{[PtL_2(NH_3)_2]Cl_2} - \Lambda_{[PtL_2(NH_3)Cl]Cl}) \, . \, [PtL_2(NH_3)_2^{2+}]_\infty \exp(k_2' + k'_{-2})t. \quad (13)$$

From the slope of the plots of $[1/R_\infty - 1/R(t)]$ the values of $(k_2' + k'_{-2})$ could be calculated. The indicated values for a series of experiments are given in Table III. For 35° the plots $(k_2' + k'_{-2})$ *vs.* NH_3 were fitted by least squares. The intercept gave $k_2'/[NH_3] = k_{2-NH_3}$. For the limited experiments at 25° the scatter of the rates prevented evaluation of rate constants with real statisitcal significance for k_{2-NH_3} and

k_{-2} since the rates were too slow for an accurate resolution of the second ammonation from the change in the $1/R_\infty$ line.

The quantity, δ, is defined as $[(1/R_\infty-1/R(t))-(1/R_\infty-1/R(t))_2]$. If initially, before products are formed, the ammonation of *trans*–$Pt(P(C_2H_5)_3)_2Cl_2$ is described by the expression

$$\frac{d[PtL_2Cl_2]}{dt}=-k_{1-NH_3}[NH_3][PtL_2Cl_2]=k_1'[PtL_2Cl_2] \quad (14)$$

the value of k_1' is given by the equation.

$$k_1'=[\frac{d\ \ln\ \delta}{dt}]_0 \quad (15)$$

Values of k_1' determined from such slopes, extrapolated to a time of zero, are also included in Table III. The value of k_{1-NH_3} was evaluated from a linear least squares plot of k_1' *vs.* $[NH_3]$. Uncertainties in the extrapolation in the quantity, $(1/R_\infty-1/R(t))_2$, to zero time limited the accuracy of the values of k_1'. However, despite these uncertainties and the fact that values of k_1' extended over a considerable range, the fractional standard deviations for the indicated k_{1-NH_3} as shown in Table III were 25% at 25° and only about 8% at 35°. These were considerably better than those for k_{2-NH_3} and k_{-2}. However, the variations were too large to provide meaningful activation enthalpies.

Table III. Ammonation of t–$Pt(P(C_3H_5)_3)_2Cl_2$.

$[Pt(P(C_2H_5)_3)_2Cl_2]_0$ mM	$[NH_3]_0$ M	KCl mM	$10^5\times k_1'$ sec^{-1}	$10^5(k_2'+k'_{-2})$ sec^{-1}
		25°		
0.441	0.142	10	3.7	0.333
.874	.814	10	21.1	1.39
.664	1.02	10	24.5	2.34
.334	1.22	10	30.4	2.18
.812	1.26	10	33.5	2.74
$k_{1-NH_3}=k_1'/[NH_3]=2.5\pm0.6\times10^{-4}M^{-1}sec^{-1}$				
$k_{2-NH_3}=2\pm.3\times10^{-5}M^{-1}sec^{-1}$, $k_{-2}=0\pm.3\times10^{-4}M^{-1}sec^{-1}$				
		35°		
.642	.0409	10	2.77	0.623
.282	.082	10	5.09	—
.643	.0835	10	5.23	1.18
.644	.180	10	11.1	1.23
.593	.364	10	24.8	1.50
.292	.445	10	30.8	2.18
.627	.604	10	43.3	2.02
.623[a]	.282	10	19.6	1.30
.639[b]	.357	10	30.2	1.77
.644	.320	30	27.8	3.79
$k_{1-NH_3}=7.0\pm.3\times10^{-4}M^{-1}sec^{-1}$				
$k_{2-NH_3}=2.2\pm.6\times10^{-5}M^{-1}sec^{-1}$, $k_{-2}=9\pm2\times10^{-4}M^{-1}sec^{-1}$				

[a] Solution aged 12 hrs before addition of NH_3. [b] Solution contained 2% H_2O.

Attempts to provide for complete characterization of the kinetics were unsuccessful. For this effort, in addition to reactions 1 and 2 the following processes were added to provide for autocatalysis.

$$Y+PtL_2Cl_2 \rightarrow Z;\ \ Rate=k_3[Y][PtL_2Cl_2] \quad (16)$$

and

$$Z+NH_3 \rightarrow PtL_2(NH_3)Cl^++Cl^-+Y;\ \ \ Rate=k_4[Z][NH_3]. \quad (17)$$

Such a mechanism to provide autocatalysis was suggested by the dimeric transition state found for the exchange of the bromide ligands of $PtBr_4^{2-}$ with free Br^-. Both $PtL_2NH_3Cl^+$ and $PtL_2(NH_3)_2^{2+}$ were tested for Y in the mechanism. Integration of the rate equations were performed numerically for trial sets of rate constants. Although the conductance change of any one experiment could be duplicated, it was not possible to find a set of rate constants and reasonable ionic conductances which would satisfactorily describe all the experiments over the range of complex concentrations.

Comparison of Reaction Rates. Values of k_{1-NH_3}, indicated as k_{NH_3}, are collected in Table IV for each of the compounds together with the second order rate constants for chloride replacement by chloride ligands and the first order solvation rate constants.

Data for the aqueous system for t–$Pt(NH_3)_2Cl_2$ are included for comparison. A surprising feature of the results is the close similarity in the second order ammonation rate constants in methanol. There is the uncertainty in the k_{NH_3} for $Pt(P(C_2H_5)_3)_2Cl_2$ because the kinetics were not fully characterized and one suspects that the value may perhaps be lower than the indicated value of 7×10^{-4} M^{-1} sec^{-1} in view of the differences between k_{Cl} and k_s for this complex. However, the values of k_{NH_3} for t–$Pt(P(C_2H_5)_3)(NH_3)Cl_2$ and t–$Pt(NH_3)_2Cl_2$ are very similar. One must conclude that the *cis*-neighbor provides very little influence on the ammonation despite the differences in k_{Cl} and k_s. It is interesting that there is so large a difference in k_{NH_3} for t–$Pt(NH_3)_2Cl_2$ between H_2O and CH_3OH whereas k_s is very similar. It is also to be noted that in each case when the *trans*-chloride has been replaced by an NH_3, the ammonation rate is reduced by about an order of magnitude in accordance with the difference in the *trans* directive properties of Cl^- and NH_3.

Table IV. Ammonation, solvation and chloride exchange rate constants for PtL_2Cl_2 at 35°.

Complex	Ionis Strength(M) Solvent	k_{NH_3} M^{-1} sec^{-1}	k_{Cl} $M^{-1}sec^{-1}$	k_s sec^{-1}
t–$Pt(P(C_2H_5)_3)_2Cl_2$	0.01/CH_3OH	7×10^{-4}?	1.2×10^{-4} [a]	1×10^{-7}
t–$Pt(P(C_2H_5)_3)(NH_3)_3)Cl_2$	.01/CH_3OH	1.4×10^{-3}	1.7×10^{-3} [a]	1.3×10^{-5}
t–$Pt(NH_3)_2Cl_2$	.01/CH_3OH	1.1×10^{-3}	—	1.3×10^{-4}
t–$Pt(NH_3)_2Cl_2$	.32/H_2O	1.1×10^{-2}	2.3×10^{-3} [b]	9.8×10^{-5} [b]

[a] Reference 4. [b] Reference 6a.

The finding that the ammonation reaction of *t*–Pt$(P(C_2H_5)_3)_2Cl_2$ was not described by a simple kinetics law is but one more anomaly in the kinetics for ligand substitution reaction for the square planar platinum(II) complexes which have been discussed previously.[3] The behavior of *t*–$Pt(P(C_2H_5)_3)_2Cl_2$ is certainly not in line with that of other closely related complexes and probably reflects steric effects resulting from the two phosphine ligands in the complex. It is apparent that the unravelling of the kinetics of *t*–$Pt(P(C_2H_5)_3)_2Cl_2$ towards ligand substitution reactions will be a formidable task.

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