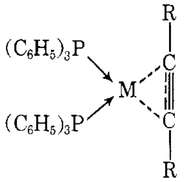
Recently one-electron semiempirical molecular orbital calculations were performed[26,27] on a series of platinum–acetylene and –olefin complexes in order to ascertain the mode of bonding and to explain the physical properties of the complexes. Calculations were performed for two configurations, planar and pseudotetrahedral. The calculations clearly illustrate that the complexes are best represented by three-coordinate platinum(0) with dp^2 hybridization in the planar case and d^2p hybridization in the pseudotetrahedral case. A bonding scheme, derived with the aid of group theory, that is consistent with the molecular orbital calculations is shown in Figure 4.

Greaves, Lock, and Maitlis[6] have come to the same conclusion about the bonding in acetylene complexes based upon molecular orbital arguments and they proposed that the complexes should best be represented by



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a formula which appears to be the least misleading.

The calculations indicate that upon coordination the acetylenic hydrogen becomes negatively charged which is in accordance with the observation that reaction of I with acetylenes in the presence of methanol, ethanol, or water yields type A complexes whereas in the presence of acetic acid type B complexes are formed.

The planar and pseudotetrahedral configurations were found to differ only slightly in energy. Thus the complexity of the C≡C—H resonance in the pmr spectra might possibly be explained by the presence of both forms in solution.[28] Further work along these lines is now in progress.

Acknowledgment.—We thank Dr. M. Gordon and Dr. L. C. Cusachs for their helpful and stimulating discussions concerning this work and Mr. Gordon Boudreaux for obtaining the pmr spectra. The financial support of the Esso Research Laboratories, Humble Oil and Refining Co., Baton Rouge, La., is gratefully acknowledged. We appreciate the assistance provided by the National Science Foundation through Chemistry Research Instrument Grants GP-1690, GP-5203, GP-6915, and GP-8237.

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[26] J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *Chem. Commun.*, 1019(1969).

[27] J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Am. Chem. Soc.*, in press.

(28) Note Added in Proof.—The acetylene in these complexes exchanges slowly[6,18,20] according to the reaction

$$Pt[(C_6H_5)_3P]_2(RC_2H) + CDCl_3 \longrightarrow Pt[(C_6H_5)_3P]_2Cl(CDCl_2) + RC_2H$$

as shown by the slow appearance of peaks attributable to free acetylene.

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cis and Charge Effects in Platinum(II)-Catalyzed Substitution Reactions of Platinum(IV) Complexes

By SUSAN G. BAILEY and RONALD C. JOHNSON

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Reactions of the type *trans*-$Pt(NH_3)_4Cl_2^{2+}$ + $Pt(dien)A^{n+}$ + $2Br^-$ → *trans*-$Pt(dien)ABr_2^{n+}$ + $Pt(NH_3)_4^{2+}$ + $2Cl^-$ and $Pt(dien)Br^+$ + *trans*-$Pt(dien)ACl_2^{n+}$ + $2Br^-$ → *trans*-$Pt(dien)Br_3^+$ + $Pt(dien)A^{n+}$ + $2Cl^-$ (where A = NO_2^-, Br^-, or NH_3; n = 1 or 2; dien = diethylenetriamine) were found to have third-order rate laws, with first-order rate dependences on the reactant Pt(IV) complex, the reactant Pt(II) complex, and bromide ion concentrations. The fastest reaction was less than ten times faster than the slowest, which indicates that *cis* and charge effects are relatively minor. The relative rates parallel the ease of oxidation of $Pt(dien)A^{n+}$ and of reduction of *trans*-$Pt(dien)ACl_2^{n+}$. The rate data are interpreted in terms of a bridged inner-sphere redox mechanism involving an activated complex of the type Pt–Cl–Pt. Rate constants and activation parameters are reported. Equilibrium constants related to these reactions were studied spectrophotometrically and correlated with the rate data.

Introduction

Numerous papers have appeared in recent years concerning detailed aspects of substitution reactions of platinum(IV) cations.[1-9] For these reactions, the observed first-order rate dependence on the concentrations of the platinum(IV) complex, the entering halide ion, and a platinum(II) complex is consistent with a mechanism proposed by Basolo and Pearson[2] involving an inner-sphere two-electron transfer followed by

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[1] F. Basolo, M. L. Morris, and R. G. Pearson, *Discussions Faraday Soc.*, **29**, 80 (1960).

[2] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 35 (1961).

[3] W. R. Mason, III, and R. C. Johnson, *Inorg. Chem.*, **4**, 1258 (1965).

[4] R. C. Johnson and E. R. Berger, *ibid.*, **4**, 1262 (1965).

[5] R. R. Rettew and R. C. Johnson, *ibid.*, **4**, 1565 (1965).

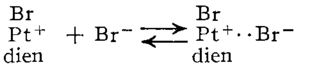
[6] W. R. Mason, III, E. R. Berger, and R. C. Johnson, *ibid.*, **6**, 248 (1967).

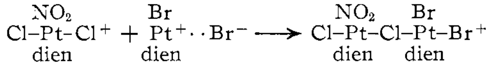
[7] R. C. Johnson and E. R. Berger, *ibid.*, **7**, 1656 (1968).

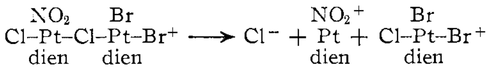
[8] A. Peloso and G. Dolcetti, *Coord. Chem. Rev.*, **1**, 100 (1966).

[9] A. Peloso and G. Dolcetti, *Gazz. Chim. Ital.*, **97**, 120 (1967).

transfer of the bridging group to the new platinum(IV) complex. The mechanism is illustrated in eq 1–3 using one of the reactions on which kinetic data are reported in this paper.


$$\overset{\text{Br}}{\underset{\text{dien}}{\text{Pt}^+}} + \text{Br}^- \rightleftharpoons \overset{\text{Br}}{\underset{\text{dien}}{\text{Pt}^+}}\cdot\cdot\text{Br}^- \qquad (1)$$


$$\text{Cl–}\overset{\text{NO}_2}{\underset{\text{dien}}{\text{Pt}}}\text{–Cl}^+ + \overset{\text{Br}}{\underset{\text{dien}}{\text{Pt}^+}}\cdot\cdot\text{Br}^- \longrightarrow \text{Cl–}\overset{\text{NO}_2}{\underset{\text{dien}}{\text{Pt}}}\text{–Cl–}\overset{\text{Br}}{\underset{\text{dien}}{\text{Pt}}}\text{–Br}^+ \qquad (2)$$


$$\text{Cl–}\overset{\text{NO}_2}{\underset{\text{dien}}{\text{Pt}}}\text{–Cl–}\overset{\text{Br}}{\underset{\text{dien}}{\text{Pt}}}\text{–Br}^+ \longrightarrow \text{Cl}^- + \overset{\text{NO}_2{}^+}{\underset{\text{dien}}{\text{Pt}}} + \text{Cl–}\overset{\text{Br}}{\underset{\text{dien}}{\text{Pt}}}\text{–Br}^+ \qquad (3)$$

This study was initiated in order to learn more about the mechanism of reactions of this kind and to study the influence of ligands *cis* to the reactive *trans* axis on the rate of such reactions. The systems chosen were picked in order first to assess the importance of the inductive and π-bonding effects of the *cis* ligands and then to evaluate the influence of their charge. Previous work gives information on these questions, but it was not possible to separate the influence of charge from inductive and π-bonding effects.

Experimental Section

Preparation of Compounds.—Tetraammineplatinum(II) chloride,[10] *trans*-dichlorotetraammineplatinum(IV) chloride,[5] and nitrodiethylenetriamineplatinum(II) nitrate[11] were prepared as described in previous papers.

Bromodiethylenetriamineplatinum(II) Bromide.—Twenty milliliters of a solution containing 0.67 g (6.4 mmol) of $N_2H_4\cdot 2HCl$ was slowly added with stirring to 6.1 g (12.6 mmol) of K_2PtCl_6 suspended in 200 ml of hot water. The reaction mixture was heated at 95° for 2 hr, cooled, and filtered to remove a small amount of platinum metal which had formed. Diethylenetriamine (25.2 mmol) was added dropwise with stirring to the red solution of K_2PtCl_4. The solution was heated at 95° until it turned light yellow (about 2 hr). The Pt(dien)BrBr was precipitated by concentration under vacuum to a smaller volume and addition of a saturated NaBr solution. The product was recrystallized from hot water, washed with cold water, and dried under vacuum at 60°; yield, 3.3 g, 57%. *Anal.* Calcd for Pt(dien)BrBr: Pt, 42.6; Br$^-$, 34.9. Found: Pt, 42.7; Br$^-$, 34.6.

Chlorodiethylenetriamineplatinum(II) chloride was made the same way as the bromodiethylenetriamineplatinum(II) bromide except the yellow solution was concentrated under vacuum until a yellow precipitate appeared (total solution volume about 10 ml). The product was recrystallized from hot water and dried overnight *in vacuo;* yield, 2.0 g, 38%. *Anal.* Calcd for Pt(dien)ClCl: Pt, 52.9; Cl$^-$, 19.2. Found: Pt, 52.0; Cl$^-$, 18.0.

Amminediethylenetriamineplatinum(II) Chloride.—To 2.04 g (5.53 mmol) of Pt(dien)Cl$_2$ dissolved in about 75 ml of water was added 20 ml of concentrated ammonia. Heating the solution 15 min at 60° followed by evaporation of the solvent under vacuum gave a white solid, Pt(dien)NH$_3$Cl$_2$. The compound was recrystallized from the minimum amount of room-temperature water by flooding with reagent acetone until the white compound precipitated. The precipitate was collected, washed with acetone, and dried *in vacuo;* yield, 1.9 g, 90%. *Anal.* Calcd for Pt(dien)NH$_3$Cl$_2$: Pt, 50.5; Cl$^-$, 18.4. Found: Pt, 50.6; Cl$^-$, 17.7.

Amminediethylenetriamineplatinum(II) bromide was prepared in the same way as the chloride salt. Starting with 1.9 g (4.15 mmol) of Pt(dien)Br$_2$, a 1.8-g (90%) yield of Pt(dien)NH$_3$Br$_2$ was obtained. *Anal.* Calcd for Pt(dien)NH$_3$Br$_2$: Pt, 41.1; Br$^-$, 33.6. Found: Pt, 41.1; Br$^-$, 33.6.

***trans*-Dichlorobromodiethylenetriamineplatinum(IV) Chloride.**—A moderately dilute ice-cold aqueous solution containing 0.477 g (2.8 mmol) of AgNO$_3$ was added with stirring to a similar solution containing 1.29 g (2.8 mmol) of Pt(dien)Br$_2$. The reaction mixture was heated on a steam bath for 30 min, filtered, centrifuged, and refiltered to rid the solution of AgBr. A 2.5-ml portion of concentrated hydrochloric acid was added to the ice-cold 150-ml solution of Pt(dien)BrNO$_3$. Chlorine gas was bubbled slowly through this stirred solution for 10 min whereupon the solution changed from colorless to yellow. The yellow solution was purged with nitrogen gas for 30 min. Solvent was stripped off under vacuum until 50 ml remained and considerable bright yellow precipitate had deposited. This was washed with acetone and dried under vacuum at 90° for 2 hr; yield, 1.3 g, 96%. *Anal.* Calcd for Pt(dien)BrCl$_2$Cl: Pt, 40.3; X$^-$, 38.4. Found: Pt, 40.2; X$^-$, 38.4. Evidence that the Br$^-$ in the square plane had not been substituted by Cl$^-$ was obtained by reducing the platinum(IV) salt to platinum(II) by means of sodium hydrogen sulfite and sulfuric acid. The spectrum of the resulting platinum(II) compound exhibited the maximum at 278 mμ characteristic of the Pt(dien)Br$^+$ ion.

***trans*-Dichloroamminediethylenetriamineplatinum(IV) Chloride.**—An ice-cold solution containing 0.72 g (1.86 mmol) of Pt(dien)NH$_3$Cl$_2$, 50 ml of water, and 1.5 ml of concentrated hydrochloric acid was chlorinated for about 5 min, whereupon the solution turned from colorless to deep yellow. The solution was evaporated to dryness under vacuum. The residue was recrystallized from hot water; yield, 0.7 g, 82%. *Anal.* Calcd for Pt(dien)NH$_3$Cl$_2$Cl$_2$: Pt, 42.7; Cl$^-$, 31.0. Found: Pt, 42.4; Cl$^-$, 30.8.

***trans*-Dichloronitrodiethylenetriamineplatinum(IV) Perchlorate.**—An ice-cold solution containing 1.1 g (2.7 mmol) of Pt(dien)NO$_2$NO$_3$, 50 ml of water, and 10 drops of concentrated hydrochloric acid was chlorinated for about 5 min. A copious light yellow precipitate appeared which disintegrated upon standing. The solution was chlorinated an additional 5 min, evaporated to 5 ml under reduced pressure, and cooled in an ice bath. Addition of a few drops of an ice-cold solution containing 1 part of concentrated perchloric acid to 2 parts of water precipitated Pt(dien)NO$_2$Cl$_2$ClO$_4$. This was recrystallized from hot water and dried under vacuum; yield, 0.82 g, 58%. *Anal.* Calcd for Pt(dien)NO$_2$Cl$_2$ClO$_4$. Pt, 37.9; Cl$^-$, 13.8. Found: Pt, 38.0; Cl$^-$, 13.5.

***trans*-Tribromodiethylenetriamineplatinum(IV) Bromide.**—A saturated aqueous solution of 0.14 g (0.34 mmol) of Pt(dien)NO$_2$NO$_3$ was added to 6 ml of concentrated hydrobromic acid heated almost to boiling. The solution soon turned orange-brown and an orange precipitated appeared. The reaction mixture was cooled in an ice bath, and the product was collected, recrystallized from hot water, and dried under vacuum; yield, 0.18 g, 85%. *Anal.* Calcd for Pt(dien)Br$_3$Br: Pt, 31.6; Br$^-$, 51.7. Found: Pt, 31.0; Br$^-$, 51.9. Evidence that Pt(dien)Br$_3$Br rather than Pt(dien)NO$_2$Br$_2$Br had been synthesized was obtained by reducing the platinum(IV) salt to platinum(II) with sodium hydrogen sulfite and sulfuric acid. An ultraviolet spectrum taken on the resulting solution showed the maximum at 278 mμ characteristic of the Pt(dien)Br$^+$ ion.

***trans*-Dibromonitrodiethylenetriamineplatinum(IV) Bromide.**—Fourteen drops of bromine were added dropwise with stirring to a solution of 0.8 g (2.0 mmol) of Pt(dien)NO$_2$NO$_3$ in 200 ml of water. The resulting golden yellow solution was stirred for 30 min and then evaporated to dryness under reduced pressure to give a golden yellow product. Recrystallization from a minimum of hot water to which was added 1 drop of concentrated hydrobromic acid produced a golden yellow precipitate which was collected and dried under vacuum at 100°; yield, 0.6 g, 50%. *Anal.* Calcd for Pt(dien)NO$_2$Br$_2$Br: Pt, 33.4; Br$^-$, 41.0. Found: Pt, 33.0; Br$^-$, 40.2.

***trans*-Dibromoamminediethylenetriamineplatinum(IV) Bromide.**—This compound was made essentially the same way as

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[10] R. N. Keller, *Inorg. Syn.*, **2**, 251 (1963).

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

the *trans*-dibromonitro compound. Starting with 0.56 g (1.2 mmol) of Pt(dien)NH_3Br_2, a yield of 0.67 g (88%) was obtained. *Anal.* Calcd for Pt(dien)$NH_3Br_2Br_2$: Pt, 30.7; Br^-, 50.3. Found: Pt, 31.1; Br^-, 49.8.

Spectral Measurements.—Ultraviolet and visible spectral measurements were made on a Cary 14 recording spectrophotometer using 1.00-cm quartz cells. All spectra of the Pt(II) and Pt(IV) compounds were run in fresh dilute aqueous solution. Slight hydrolysis was noted with some of the Pt(IV) compounds after about 24 hr. Since the spectrum of Pt(dien)BrBr was taken on fresh 2.38×10^{-3} *M* solutions, the hydrolysis noted by Martin[12,13] was not a problem. Spectra of some of the compounds were also taken in solutions which were 5×10^{-3} *M* in $HClO_4$ and 0.2 *M* in $NaClO_4$. No changes from the spectra in plain water were observed.

Kinetic Measurements.—Kinetics were followed spectrophotometrically using a Cary 14 spectrophotometer. The cell compartment of the spectrophotometer was thermostated to ±0.02°. All Pt(IV) solutions were made fresh daily. The reactions were studied in acid media under conditions such that the ratios of Pt(II) to Pt(IV) concentrations and of Br^- to Pt(IV) concentrations were greater than or equal to 50:1. Under these conditions the reactions were pseudo first order in Pt(IV). The large excess of Pt(II) also forced the reactions to go to completion with the formation of the platinum(IV) product derived from the platinum(II) reactant. Both Br^- and the Pt(II) salts absorb appreciably in the region of the ultraviolet spectrum where the largest spectral changes were observed as the reactions proceeded from the Pt(IV) reactant to the Pt(IV) product. Therefore, the reference cell always contained the same concentrations of Pt(II) salt and Br^- as were used in the reaction mixture in order to blank out these absorbances. In all cases suitably large absorbance changes (of the order of 0.5–1 absorbance unit) were observed.

In all kinetic runs from which third-order rate constants were computed, the ionic strength was controlled at 0.20 *M* with $NaClO_4$ and the hydrogen ion concentration was controlled at 5.0×10^{-3} *M* with $HClO_4$. Independent studies to determine what effect a change in ionic strength or pH would have on the observed rate constant were made for each reaction studied.

Infinite-time spectra of all kinetic runs were identical with those of the expected reaction products. The reaction of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ with Pt(dien)NO_2^+ and Br^- was followed at 237 mμ which corresponds to an absorbance maximum for Pt(dien)$NO_2Br_2^+$, the reaction of *trans*-$Pt(NH_3)_4Cl_2^+$ with Pt(dien)Br^+ and Br^- was followed at 240 mμ, an absorbance maximum for Pt(dien)Br_3^+, and the reaction of *trans*-$Pt(NH_3)_4Cl_2^+$ with Pt(dien)NH_3^{2+} and Br^- was followed at 237 mμ, an absorbance maximum for Pt(dien)$NH_3Br_2^{2+}$. Reactions of *trans*-Pt(dien)$NH_3Cl_2^{2+}$, *trans*-Pt(dien)$BrCl_2^+$, and *trans*-Pt(dien)$NO_2Cl_2^+$ with Pt(dien)Br^+ and Br^- were all followed at the 240-mμ absorbance maximum of Pt(dien)Br_3^+.

A possible complication in one kinetic study was interference by the reaction

$$\mathrm{Pt(dien)NO_2^+ + Br^- \longrightarrow Pt(dien)Br^+ + NO_2^-} \qquad (4)$$

However mixtures of Pt(dien)NO_2^+ and Br^- with concentrations similar to those used in our kinetic studies showed no absorbance changes on standing at 25° for several days. This qualitative result is consistent with rate data on related systems which are presented in the literature.[14]

The reactivity of a 10-day old Pt(dien)BrBr solution was observed to be about half that of a fresh solution. The reason for this behavior is not known, but hydrolysis should not be responsible since sufficient bromide ion was present to make the equilibrium conversion to Pt(dien)H_2O^{2+} small.[13]

Rate data were evaluated[15] by a least-squares technique utilizing a Gauss–Newton exponential fit to the equation

$$A = A_\infty + (A_0 - A_\infty)\exp(-kt)$$

where A, A_∞, and A_0 are absorbances at t, infinity, and initial time. Successive approximations are made to give A_∞, $(A_0 - A_\infty)$, and k by an iterative procedure. Absorbance *vs.* time data covering at least 3 half-lives were evaluated for all kinetic runs and excellent fit to the first-order equation resulted. Third-order rate constants were obtained by dividing the observed rate constants by the product of $[Br^-][Pt(II)]$. From the third-order rate data at three different temperatures, activation parameters were calculated.

Equilibrium Measurements.—The equilibria

$$trans\text{-}\mathrm{Pt(NH_3)_4Cl_2^{2+} + Pt(dien)NH_3^{2+}} = \mathrm{Pt(NH_3)_4^{2+}} + trans\text{-}\mathrm{Pt(dien)NH_3Cl_2^{2+}} \qquad (5)$$

and

$$trans\text{-}\mathrm{Pt(NH_3)_4Cl_2^{2+} + Pt(dien)NO_2^+} = \mathrm{Pt(NH_3)_4^{2+}} + trans\text{-}\mathrm{Pt(dien)NO_2Cl_2^+} \qquad (6)$$

were studied spectrophotometrically at 265 mμ. Initially equimolar quantities of the two reactants were mixed and the spectrum was scanned repetitively from 300 to 200 mμ at about 2-min intervals in order to determine where the maximum absorbance change would take place in going from reactants to equilibrium. Equilibrium measurements were made under kinetic conditions using $NaClO_4$ and $HClO_4$ to maintain ionic strength at 0.2 *M* and hydrogen ion concentration at 5.0×10^{-3} *M*, respectively. Thus either the two reactants or the two products were mixed at equimolar concentration and their absorbance *vs.* time at the above wavelength was recorded. From this, extrapolation to A_0 (absorbance at zero time) could be made. The reactions were then allowed to sit for several days, thermostated at 25°, and examined periodically to determine when they had come to equilibrium. In all cases absorbances remained constant over a 24-hr period before A_{eq} (absorbance at equilibrium) values were read. Equilibrium constants could then be computed using

$$K = \left(\frac{A_0(\text{reactants}) - A_{eq}}{A_0(\text{products}) - A_{eq}}\right)^2 \qquad (7)$$

In this equation A_0(reactants) is the experimentally measured absorbance of a mixture of reactants extrapolated to the time of mixing; A_0(products) is the absorbance of a mixture of the pure products at the time of mixing. Equation 7 can be readily derived. It is valid only for studies in which the concentrations of platinum(IV) and platinum(II) reactants are equal.

In addition the equilibria

$$trans\text{-}\mathrm{Pt(dien)Br_3^+ + Pt(dien)NH_3^{2+}} = \mathrm{Pt(dien)Br^+} + trans\text{-}\mathrm{Pt(dien)NH_3Br_2^{2+}} \qquad (8)$$

and

$$trans\text{-}\mathrm{Pt(dien)NO_2Br_2^+ + Pt(dien)NH_3^{2+}} = \mathrm{Pt(dien)NO_2^+} + trans\text{-}\mathrm{Pt(dien)NH_3Br_2^{2+}} \qquad (9)$$

were studied at 280 and 290 mμ, respectively. By superimposing the ultraviolet spectra in the region 400–200 mμ of equal concentrations of the six platinum complexes, these wavelengths were found to be the most suitable for studying these equilibria. The concentrations of bromide salts of the platinum complexes necessary to give suitably large absorbance changes in going from reactants or products to equilibrium were such that equilibrium was attained in all cases within less than 10 sec. Therefore to obtain A_0 values for these systems, the molar absorptivities for each of the complexes used at the wavelength of the study were measured several times and the A_0 values for each component were computed from $A_0 = \epsilon C_0$. Thus in (8), for example, A_0(reactants) = A_0(Pt(dien)Br_3^+) + A_0(Pt-

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[12] D. S. Martin, Jr., and L. Bahn, *Inorg. Chem.*, **6**, 1653 (1967).

[13] J. E. Teggins and D. S. Martin, Jr., *ibid.*, **6**, 1003 (1967).

[14] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 33–36.

[15] Computation was performed on an IBM 1410 computer in the Emory University Computer Center.

(dien)NH_3^{2+}). Values of A_{eq} for (8) and (9) were obtained in a manner analogous to those for (5) and (6). Equation 7 could then be used to calculate equilibrium constants for (8) and (9).

For reactions 5, 6, and 8 the values of A_{eq} obtained by studying the reactions in both the forward and reverse directions were in excellent agreement. For reaction 9 the discrepancy in A_{eq} determined from the two directions was 0.067 in a total absorbance change of 1.086. A number of samples of all reactants and products were used, but we were unable to eliminate this discrepancy which is almost certainly due to an impurity in the *trans*-Pt(dien)$NO_2Br_2^+$ salts used. This discrepancy certainly limits the reliability of the value of the equilibrium constant for this reaction; however we feel it is sufficiently accurate to indicate at least semiquantitatively the stability of these compounds. The K's in all cases were evaluated using the differences between absorbances of pure complexes and the equilibrium value obtained from them, rather than using an average A_{eq} in both the numerator and denominator. One reason for using this procedure was that these differences were similar for most of the samples tried even though individual absorbances and equilibrium absorbances did not agree very well in some cases.

For all of the equilibrium constants several sets of data were collected. The standard deviations resulting from the comparison of these data sets are presented in Table III. The value for K(eq 9) is certainly less reliable than this type of analysis suggests.

Results

Rate data for the reactions studied are presented in Table I. Although the net reaction observed in each case was the substitution of two chloride ions by two bromide ions, previous experience with similar systems[5] indicates the replacement of the first chloride is rate determining. Hence all of the rate constants measure the rate of replacement of the first chloride. This is also the only model consistent with the excellent pseudo-first-order kinetics observed for these reactions. The rate data for all reactions studied are consistent with the general rate law

$$\text{rate} = k[\text{Pt(IV)}][\text{Pt(II)}][\text{Br}^-] \qquad (10)$$

Many of the rate constants reported are average values from several experiments; rate constants from repeated experiments differed from one another by only a few per cent. The rate constants are insensitive to changes in $[H^+]$ over the range of 0.005–0.11 M. Rate data which indicate the influence of ionic strength are reported.

Table II summarizes the third-order rate constants at 24.2° and the activation parameters for the reactions studied.

Table III presents the results of equilibrium studies on reactions 5, 6, 8, and 9.

Visible and ultraviolet spectral bands and intensities for the Pt(dien)Cl^+, Pt(dien)Br^+, Pt(dien)NO_2^+, Pt(dien)NH_3^{2+}, *trans*-Pt(dien)$BrCl_2^+$, *trans*-Pt(dien)-Br_3^+, *trans*-Pt(dien)$NO_2Cl_2^+$, *trans*-Pt(dien)$NO_2Br_2^+$, *trans*-Pt(dien)$NH_3Cl_2^{2+}$, and *trans*-Pt(dien)$NH_3Br_2^{2+}$ cations are tabulated in Table IV. The spectra were obtained in dilute aqueous solutions but identical results were obtained in a solution 5.0×10^{-3} M in $HClO_4$ and 0.20 M in $NaClO_4$.

Discussion

The reactions reported in this paper involve the oxidation of platinum(II) complexes by platinum(IV) complexes. In terms of mechanism these reactions appear to be very similar to platinum(II)-catalyzed substitution of platinum(IV) complexes. These reactions were chosen for study since they indicate the influence on reaction rate of the ligands *cis* to the reactive *trans* axis and of changes in the charge of the reacting platinum complexes. Changing ligands *cis* to the reactive *trans* axis produced only small effects on the rates of the reactions studied. In one series of reactions studied (eq 11) only one *cis* ligand in the platinum(IV) reactant was varied ($X = NO_2^-$, Br^-, NH_3; $n = 1, 2$). The relative rates at 24.2° were in the order: NO_2^- (5.4) > Br^- (1.2) > NH_3 (1.0). The other series (eq 12) involved only the change of one ligand in the platinum(II) reactant ($X = NO_2^-$, Br^-, NH_3; $n = 1, 2$). The relative rates were in the order: NH_3 (3.3) > Br^- (1.1) > NO_2^- (1.0). The reactivity orders in the two series are reversed. This suggests that the rates of these reactions are appreciably influenced by the relative stabilities of the reactants and products. It would follow then that NO_2^- stabilizes platinum(II) with respect to platinum(IV); ammonia stabilizes platinum(IV) *vs.* platinum(II); and bromide ion is intermediate. This suggestion has been verified by equilibrium studies (see Table III). The reactivity order parallels the π-accepting abilities of the *cis* ligands. It is known that π acceptors form very stable platinum(II) complexes, whereas it seems certain that platinum(IV) is a much poorer π donor. The reactivity order is not in line with the σ-bonding ability as measured for example by the pK_a's of NH_4^+, HNO_2, and HBr.

$$trans\text{-Pt(dien)}XCl_2^{n+} + \text{Pt(dien)}Br^+ + 2Br^- \longrightarrow trans\text{-Pt(dien)}Br_3^+ + \text{Pt(dien)}X^{n+} + 2Cl^- \qquad (11)$$

$$trans\text{-Pt}(NH_3)_4Cl_2^{2+} + \text{Pt(dien)}X^{n+} + 2Br^- \longrightarrow trans\text{-Pt(dien)}XBr_2^{n+} + \text{Pt}(NH_3)_4^{2+} + 2Cl^- \qquad (12)$$

We have then demonstrated that fairly marked changes in the inductive and π-bonding properties of *cis* ligands produce only small effects on the rate of platinum(II)-catalyzed reactions. It should be noted however that previous workers have demonstrated that the size of *cis* ligands is very important.[1] The *trans*-dichlorobis (tetramethylethylenediamine)platinum (IV) cation exchanges chloride at a negligibly slow rate under conditions at which chloride exchange is rapid with the ethylenediamine complex.

Our rate studies also show that the magnitude of the charge on the platinum(IV) or platinum(II) complex has little influence on the rates of these platinum(II)-catalyzed reactions. Since the inductive and mesomeric effects of the *cis* ligands have been shown to be small, the small effect of charge cannot be attributed to coincidental cancelling of large charge and *cis* effects.

TABLE I

RATE DATA

$\mathrm{Pt(dien)NO_2Cl_2^+ + Pt(dien)Br^+ + Br^- \longrightarrow Pt(dien)Br_2Cl^+ + Pt(dien)NO_2^+ + Cl^-}$

10^3[Pt(dien)Br$^+$], M	10^3k_{obsd},[a] sec^{-1}	k_3, M^{-2} sec^{-1}	10^3[Pt(dien)Br$^+$], M	10^3k_{obsd},[a] sec^{-1}	k_3, M^{-2} sec^{-1}
24.2°			34.2°		
2.38	5.2	922	0.60	1.81[b]	1270
25.0°			1.19	3.6	1258
0.60	1.34[b]	940	2.38	7.3	1280
1.19	2.6	926			
1.19	5.3[c]	936			
1.19	10.6[d]	932	43.5°		
2.38	5.3	928	0.30	1.24	1737
2.38	5.3[e]	928	0.60	2.3[b]	1608
2.38	7.0[f]	1232	1.19	4.6	1632

$\mathrm{Pt(dien)BrCl_2^+ + Pt(dien)Br^+ + Br^- \longrightarrow Pt(dien)Br_2Cl^+ + Pt(dien)Br^+ + Cl^-}$

10^4[Pt(dien)Br$^+$], M	10^3k_{obsd},[g] sec^{-1}	k_3, M^{-2} sec^{-1}	10^4[Pt(dien)Br$^+$], M	10^3k_{obsd},[g] sec^{-1}	k_3, M^{-2} sec^{-1}
24.2°			33.8°		
1.76	0.31	211	1.76	0.46	313
3.53	0.32[h]	206	3.53	0.89	302
3.53	0.61	202	7.06	1.68	284
3.53	1.13[i]	195			
7.06	1.19	200	43.0°		
7.06	0.44[j]	228	0.86	0.30	416
			1.78	0.62	412
			3.53	1.21	408
			3.43	1.42[k]	494
			3.43	1.26[l]	437

$\mathrm{Pt(dien)NH_3Cl^{2+} + Pt(dien)Br^+ + Br^- \longrightarrow Pt(dien)Br_2Cl^+ + Pt(dien)NH_3^{2+} + Cl^-}$

10^3[Pt(dien)Br$^+$], M	10^3k_{obsd},[m] sec^{-1}	k_3, M^{-2} sec^{-1}	10^3[Pt(dien)Br$^+$], M	10^3k_{obsd},[m] sec^{-1}	k_3, M^{-2} sec^{-1}
24.2°			33.8°		
1.19	1.92[n]	170	1.19	1.53	271
2.4	0.96[o]	170	2.4	3.0	266
2.4	1.98	175	4.8	6.3	277
2.4	3.8[n]	167			
2.4	3.8[n,p]	167	43.0°		
2.4	3.9[n,q]	172	0.60	1.14[r]	400
4.8	7.5[n]	165	1.19	2.3	410
			2.4	4.6	406

$\mathrm{Pt(NH_3)_4Cl_2^{2+} + Pt(dien)NH_3^{2+} + Br^- \longrightarrow Pt(dien)NH_3ClBr^{2+} + Pt(NH_3)_4^{2+} + Cl^-}$

10^3[Pt(dien)NH$_3^{2+}$], M	10^3k_{obsd},[s] sec^{-1}	k_3, M^{-2} sec^{-1}	10^3[Pt(dien)NH$_3^{2+}$], M	10^3k_{obsd},[s] sec^{-1}	k_3, M^{-2} sec^{-1}
24.2°			33.8°		
0.60	1.11[t]	388	0.60	1.61[t]	563
1.19	1.15[u]	406	1.19	3.2	558
1.19	2.2	389	2.38	6.5	572
1.19	4.4[v]	392			
1.19	2.5[v,w]	221	43.0°		
1.19	4.4[v,x]	390	0.60	2.2[t]	776
2.38	4.5	402	1.19	4.3	752

$\mathrm{Pt(NH_3)_4Cl_2^{2+} + Pt(dien)Br^+ + Br^- \longrightarrow Pt(dien)Br_2Cl^+ + Pt(NH_3)_4^{2+} + Cl^-}$

10^3[Pt(dien)Br$^+$], M	10^3k_{obsd},[y] sec^{-1}	k_3, M^{-2} sec^{-1}	10^3[Pt(dien)Br$^+$], M	10^3k_{obsd},[y] sec^{-1}	k_3, M^{-2} sec^{-1}
24.2°			33.8°		
1.19	1.09[z]	124	1.19	1.13[ee]	198
2.4	1.16[aa]	136	2.4	2.2[ee]	195
2.4	2.09	123	4.8	4.3[ee]	191
2.4	1.95[bb]	114			
2.4	2.04[cc]	120	43.0°		
2.4	4.4[dd]	128	1.19	0.84[ff]	296
4.8	4.7	138	2.4	1.70[ff]	300

$\mathrm{Pt(NH_3)_4Cl_2^{2+} + Pt(dien)NO_2^+ + Br^- \longrightarrow Pt(dien)NO_2BrCl^+ + Pt(NH_3)_4^{2+} + Cl^-}$

10^3[Pt(dien)NO$_2^+$], M	10^3k_{obsd},[gg] sec^{-1}	k_3, M^{-2} sec^{-1}	10^3[Pt(dien)NO$_2^+$], M	10^3k_{obsd},[gg] sec^{-1}	k_3, M^{-2} sec^{-1}
24.2°			33.8°		
0.60	1.14	119	0.60	1.88	196
1.20	0.166[hh]	115	1.21	3.7	190
1.20	0.56[ii]	115			
1.20	1.16[jj]	120	43.0°		
1.20	2.3	119	0.60	1.43[jj]	298
1.20	2.4[kk]	121	1.21	2.8[jj]	286
1.20	2.3[ll]	118			

[a] [*trans*-Pt(dien)NO$_2$Cl$_2^+$] = 2.4×10^{-5} M, [H$^+$] = 5.0×10^{-3} M, $\mu = 0.20$ M, [Br$^-$] = 2.4×10^{-3} M. [b] [*trans*-Pt(dien)NO$_2$Cl$_2^+$] = 1.19×10^{-5} M. [c] [Br$^-$] = 4.8×10^{-3} M. [d] [Br$^-$] = 9.5×10^{-3} M. [e] [H$^+$] = 0.11 M. [f] $\mu = 0.013$ M. [g] [*trans*-Pt(dien)BrCl$_2^-$] = 2.1×10^{-5} M, [H$^+$] = 5.0×10^{-3} M, $\mu = 0.20$ M, [Br$^-$] = 8.4×10^{-3} M. [h] [Br$^-$] = 4.4×10^{-3} M. [i] [Br$^-$] = 16.4×10^{-3} M. [j] [Br$^-$] = 2.7×10^{-3} M. [k] $\mu = 0.013$ M. [l] [H$^+$] = 0.10 M. [m] [*trans*-Pt(dien)NH$_3$Cl$_2^{2+}$] = 2.4×10^{-5} M, [H$^+$] = 5.0×10^{-3} M, $\mu = 0.20$ M, [Br$^-$] = 4.8×10^{-3} M. [n] [Br$^-$] = 9.52×10^{-3} M. [o] [Br$^-$] = 2.4×10^{-3} M. [p] $\mu = 0.013$ M. [q] [H$^+$] = 0.11 M. [r] [Pt(dien)NH$_3$Cl$_2^{2+}$] = 1.19×10^{-5} M. [s] [Pt(NH$_3$)$_4$Cl$_2^{2+}$] = 2.4×10^{-5} M, [H$^+$] = 5.0×10^{-3} M, μ = 0.20 M, [Br$^-$], 4.8×10^{-3} M. [t] [Pt(NH$_3$)$_4$Cl$_2^{2+}$] = 1.2×10^{-5} M. [u] [Br$^-$] = 2.4×10^{-3} M. [v] [Br$^-$] = 9.5×10^{-3} M. [w] μ = 0.013 M. [x] [H$^+$] = 0.11 M. [y] [Pt(NH$_3$)$_4$Cl$_2^{2+}$] = 2.4×10^{-5} M, [H$^+$] = 5.0×10^{-3} M, $\mu = 0.20$ M, [Br$^-$] = 7.2×10^{-3} M. [z] [Br$^-$] = 7.4×10^{-3} M. [aa] [Br$^-$] = 3.6×10^{-3} M. [bb] $\mu = 0.013$ M. [cc] [H$^+$] = 0.11 M. [d] [Br$^-$] = 14.3×10^{-3} M. [ee] [Br$^-$] = 4.8×10^{-3} M. [ff] [Br$^-$] = 2.4×10^{-3} M. [gg] [Pt(NH$_3$)$_4$Cl$_2^{2+}$] = 1.20×10^{-5} M, [H$^+$] = 5.0×10^{-3} M, $\mu = 0.20$ M, [Br$^-$] = 16.0×10^{-3} M. [hh] [Br$^-$] = 1.20×10^{-3} M. [ii] [Br$^-$] = 4.0×10^{-3} M. [jj] [Br$^-$] = 8.0×10^{-3} M. [kk] $\mu = 0.013$ M. [ll] [H$^+$] = 0.11 M.

Several sets of data from ref 1 (Table V) also suggest that charge plays a minor role in determining the rate of these platinum(II)-catalyzed reactions. That the rate constant of reaction 13 ($k = 172$ M^{-2} sec^{-1} at 25.0°)[16] is

$$\mathit{trans}\text{-}\mathrm{Pt(en)(NO_2)_2Cl_2 + 2Br^- \longrightarrow}\ \mathit{trans}\text{-}\mathrm{Pt(en)(NO_2)_2Br_2 + 2Cl^-} \quad (13)$$

similar to those found in this study further supports this claim.

The reactivities of these very similar complexes *trans*-Pt(NH$_3$)$_4$Cl$_2^{2+}$, *trans*-Pt(en)$_2$Cl$_2^{2+}$, and *trans*-Pt(dien)NH$_3$Cl$_2^{2+}$ and Pt(NH$_3$)$_4^{2+}$, Pt(en)$_2^{2+}$, and Pt(dien)NH$_3^{2+}$ are all different, and the magnitudes of the rate differences between the chelated and unchelated complexes are as great or greater than those observed

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(16) A. Syamal, private communication.

TABLE II

RATE CONSTANTS AT 24.2° AND ACTIVATION PARAMETERS

Pt(IV) reactant	Pt(II) reactant	ΔH^*,[a] kcal/mol	ΔS^*,[b] cal/mol deg	$10^{-2}k_3$, M^{-2} sec^{-1}
$Pt(dien)NO_2Cl_2^+$	$Pt(dien)Br^+$	5.0	−28	9.3
$Pt(dien)BrCl_2^+$	$Pt(dien)Br^+$	6.2	−27	2.0
$Pt(dien)NH_3Cl_2^{2+}$	$Pt(dien)Br^+$	8.0	−21	1.7
$Pt(NH_3)_4Cl_2^{2+}$	$Pt(dien)NH_3^{2+}$	5.9	−27	4.0
$Pt(NH_3)_4Cl_2^{2+}$	$Pt(dien)Br^+$	7.6	−23	1.3
$Pt(NH_3)_4Cl_2^{2+}$	$Pt(dien)NO_2^+$	8.4	−21	1.2
$Pt(NH_3)_4Cl_2^{2+}$	$Pt(NH_3)_4^{2+}$	7.5	−24	1.1[5]

[a] The largest standard deviation in ΔH^* was less than 0.4 kcal/mol. [b] The largest standard deviation in ΔS^* was less than 1.2 cal/mol deg.

TABLE III

EQUILIBRIUM CONSTANTS[a] AT 25.0°

$K(\text{eq } 5) = [Pt(dien)NH_3Cl_2^{2+}][Pt(NH_3)_4^{2+}]/[Pt(NH_3)_4Cl_2^{2+}][Pt(dien)NH_3^{2+}]$

A_0(reactants)	A_{eq}(reactants)	A_{eq}(products)	A_0(products)	K[b]
0.655	0.935	0.934	1.059	5.0 ± 0.3

$K(\text{eq } 6) = [Pt(dien)NO_2Cl_2^+][Pt(NH_3)_4^{2+}]/[Pt(NH_3)_4Cl_2^{2+}][Pt(dien)NO_2^+]$

A_0(reactants)	A_{eq}(reactants)	A_{eq}(products)	A_0(products)	K[c]
0.818	1.158	1.161	1.754	0.33 ± 0.05

$K(\text{eq } 8) = [Pt(dien)NH_3Br_2^{2+}][Pt(dien)Br^+]/[Pt(dien)Br_3^+][Pt(dien)NH_3^{2+}]$

A_0(reactants)	A_{eq}(reactants)	A_{eq}(products)	A_0(products)	K[d]
1.540	0.986	0.968	0.577	2.0 ± 0.2

$K(\text{eq } 9) = [Pt(dien)NH_3Br_2^{2+}][Pt(dien)NO_2^+]/[Pt(dien)NO_2Br_2^+][Pt(dien)NH_3^{2+}]$

A_0(reactants)	A_{eq}(reactants)	A_{eq}(products)	A_0(products)	K[e]
1.766	1.025	0.958	0.680	7

[a] $[H^+] = 5.0 \times 10^{-3}\ M$; $[NaClO_4] = 0.20\ M$. [b] $[Pt(II)] = [Pt(IV)] = 9.44 \times 10^{-4}\ M$; $[Cl^-] = 1.89 \times 10^{-3}\ M$. [c] $[Pt(II)] = [Pt(IV)] = 7.94 \times 10^{-4}\ M$; $[Cl^-] = 2.10 \times 10^{-3}\ M$. [d] $[Pt(II)] = [Pt(IV)] = 7.56 \times 10^{-4}\ M$; $[Br^-] = 4.80 \times 10^{-3}\ M$. [e] $[Pt(II)] = [Pt(IV)] = 7.56 \times 10^{-4}\ M$; $[Br^-] = 2.27 \times 10^{-3}\ M$.

TABLE IV

VISIBLE AND ULTRAVIOLET SPECTRAL BANDS[a]

Compound	λ_{max} mμ, (ϵ max)		
Pt(dien)ClCl	330–308 (44 sh)	270 (262)	
Pt(dien)BrBr	323 (64 sh)	278 (243)	
$Pt(dien)NO_2NO_3$	253 (1642)		
$Pt(dien)NH_3Br_2$	285 (58)		
trans-$Pt(dien)BrCl_2Cl$	273 (2520)	214 (2.74×10^4)	
trans-$Pt(dien)BrBr_2Br$	350 (1394)	240 (3.39×10^4)	
trans-$Pt(dien)NO_2Cl_2Cl$	287 (2338 sh)	240 (1.08×10 sh)	208 (3.98×10^4)
trans-$Pt(dien)NO_2Br_2Br$	327 (1718)	237 (5.01×10^4)	
trans-$Pt(dien)NH_3Cl_2Cl_2$	333 (130)	266 (1125)	207 (3.82×10^4)
trans-$Pt(dien)NH_3Br_2Br_2$	325 (1510)	237 (4.14×10^4)	

[a] sh, shoulder.

when $Pt(dien)Br^+$ is used as a reactant in place of $Pt(dien)NO_2^+$ or $Pt(dien)NH_3^{2+}$. It has been suggested[1] that *trans*-$Pt(NH_3)_4Cl_2^{2+}$ reacts more slowly than *trans*-$Pt(en)_2Cl_2^{2+}$ due to steric restraints resulting from the greater solvation of the ammonia complex. Our studies show *trans*-$Pt(NH_3)_4Cl_2^{2+}$ reacts more slowly than *trans*-$Pt(dien)NH_3Cl_2^{2+}$, and $Pt(NH_3)_4^{2+}$ reacts more slowly than $Pt(dien)NH_3^{2+}$. The same explanation would seem pertinent in this case. It should be noted that our equilibrium studies indicate that *trans*-$Pt(dien)NH_3Cl_2^{2+}$ is more stable with respect to $Pt(dien)NH_3^{2+}$ than is *trans*-$Pt(NH_3)_4Cl_2^{2+}$ *vs.* $Pt(NH_3)_4^{2+}$. Therefore the significantly smaller reactivity of $Pt(NH_3)_4^{2+}$ *vs.* $Pt(dien)NH_3^{2+}$ (and presumably also $Pt(en)_2^{2+}$) at least in part is due to its smaller reducing power. Since *trans*-$Pt(NH_3)_4Cl_2^{2+}$ is a better oxidizing agent than *trans*-$Pt(dien)NH_3Cl_2^{2+}$, its slightly slower reactions must be due to another factor such as solvation. It is interesting that chelation produces greater rate effects in these systems than do changes in complex charge or the use of *cis* ligands with appreciably different inductive and π-bonding properties.

The effect of ionic strength on the rates of the studied reactions shows a regular trend with respect to charges on the reacting ions. In the reaction in which the sum of the charges of the reacting ions was +3, the rate almost doubled as the ionic strength was increased from 0.013 to 0.10. In the three reactions in which the charge sum was +2 the effect of ionic strength changes was small. In the two reactions in which the charge sum was +1, the reaction rate decreased by 25% as the ionic strength increased from 0.013 to 0.10. Although the ionic strength effects will depend on the rate law and not the reaction mechanism, using the mechanism in eq 1–3, it is possible to rationalize this behavior. In preequilibrium step 1 in the reactions studied positive and negative ions combine; as a consequence the value of K for this step should decrease as the ionic strength increases. An enhanced

TABLE V
RATE DATA ON CHLORIDE EXCHANGE WHICH INDICATE THE INFLUENCE OF CHARGE ON REACTION RATE[1]

Platinum(IV) reactant	Platinum(II) catalyst	$k_3(25°)$, $M^{-2}\ sec^{-1}$
$Pt(NH_3)_5Cl^{3+}$	$Pt(NH_3)_4^{2+}$	0.00065[a]
cis-$Pt(NH_3)_4Cl_2^{2+}$	$Pt(NH_3)_4^{2+}$	0.0028[a]
trans-$Pt(NH_3)_4Cl_2^{2+}$	$Pt(NH_3)_4^{2+}$	6.3
trans-$Pt(NH_3)_3Cl_3^{+}$	$Pt(NH_3)_4^{2+}$	22
trans-$Pt(NH_3)_3Cl_3^{+}$	$Pt(NH_3)_3Cl^{+}$	30

[a] Although these are labeled chloride-exchange reactions, an ammonia molecule is replaced by chloride in a slow reaction which is then followed by exchange of chloride in the new product.

TABLE VI
A CORRELATION BETWEEN EQUILIBRIUM AND RATE CONSTANTS FOR SOME REACTIONS OF PLATINUM(IV) COMPLEXES

$$trans\text{-}Pt(NH_3)_4ClX^{(3-n)+} + Cl^- \longrightarrow trans\text{-}Pt(NH_3)_4Cl_2^{2+} + X^{n-}$$

X	$K(25°)$	$k(25°)$, $M^{-2}\ sec^{-1}$	Ionic strength	Ref
Pyridine	8.2	8	0.20	7
Br^-	0.06	6.3	0.20	5
SCN^-	0.0028[a]	2.7	1.10	6
Ammonia	0.0014	0.0012	0.32	3, 4

[a] At 35.0°.

rate is expected to result from the rate-determining step 2 as the ionic strength is raised for the one reaction in which two positively charged species combine to form an activated complex with charge +3. This effect apparently overrides the reverse effect due to the preequilibrium. In the other five reactions the "ion pair" formed in step 1 is uncharged, and little ionic strength influence is expected for ion–molecule reactions. The ionic strength effect on the preequilibrium step thus determines the result for the reactions in which two +1 ions and one −1 ion react. It is not surprising that the reactions of intermediate charge type (total charge +2) exhibit intermediate (negligible) ionic strength effects.

In the reactions reported in this article the reaction rates correlate with the relative stabilities of reactants and products. Previous studies on platinum(II)-catalyzed reactions of platinum(IV) complexes (Table VI) show a similar relationship. It must be admitted, however, that although the equilibrium and rate constants in this table do fall in the same order, the magnitudes of the numbers do not correlate well. A good correlation would require appreciably faster rates for the reactions in which the neutral molecules pyridine and ammonia are displaced. The correlation which exists between equilibrium and rate constants does indicate that the activated complex for these reactions is relatively symmetrical and hence resembles to some extent both reactants and products. This, not too surprisingly, seems to be particularly valid when both entering and leaving groups are halide anions. The activated complex in a reaction in which an amine is displaced by a halide anion is inherently less symmetrical.

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Transition Metal Complexes of a Cationic Phosphine Ligand[1,2]

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A monodentate phosphine which also contains a quaternary phosphorus atom in a four-member ring was synthesized and characterized. This cationic ligand, the 3-[(diphenylphosphino)methyl]-3-methyl-1,1-diphenylphosphetanium ion, abbreviated (P–P$^+$), forms the planar complexes $[Au(P\text{–}P^+)Cl_3]Cl$, $[Pd(P\text{–}P^+)_2Cl_2](ClO_4)_2$, and $Pd(P\text{–}P^+)Cl_3$ as well as the pseudotetrahedral complexes $Ni(P\text{–}P^+)X_3$ (where $X_3 = Cl_3$, $BrCl_2$, Br_2Cl) and $Co(P\text{–}P^+)X_3$ (where $X_3 = Cl_3$, Br_2Cl, I_3). The similarity of the magnetism and electronic spectral data for the $M(P\text{–}P^+)X_3$ complexes (M = Ni, Co) with those of the known pseudotetrahedral $MP(C_6H_5)_3Y_3^-$ anions (M = Ni, Co; Y = halide) indicates that the phosphine cation functions essentially as triphenylphosphine; *i.e.*, the positive charge three atoms away exerts little influence on the coordination properties of the nonquaternary phosphine group.

Introduction

Compared with the extensive number of investigations of transition metal complexes with neutral and anionic ligands, relatively few studies with positively charged ligands have been reported. In fact, the only planned efforts have been expended by Quagliano and coworkers[3-6] where they studied the coordination

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(1) This paper is based on part of the thesis submitted by D. L. Berglund to the Graduate School of The Ohio State University, March 1969, in partial fulfillment of the requirements for the Ph.D. degree.

(2) Presented at the 1st Central Regional Meeting of the American Chemical Society, Akron, Ohio, April 1968.

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