

- by F. A. Cotton and D. M. Goodgame, *J. Chem. Soc.*, 5267 (1960). No pentachlorophenylnickel complex containing perchlorato group could be isolated. Analogous results have been reported by J. M. Coronas and J. Sales, *J. Organomet. Chem.*, **94**, 107 (1975). The reaction of *trans*- o -CH₃C₆H₄Ni(PPhMe₂)₂Cl with silver perchlorate was much more complex; the precipitate of silver chloride was quickly reduced to metallic silver and no *o*-tolylnickel species could be obtained from the system.
- (6) R. Uson, J. Fornies, and S. Gouzalo, *J. Organomet. Chem.*, **104**, 253 (1976).
 - (7) R. Uson, P. Royo, and J. Gimeno, *J. Organomet. Chem.*, **72**, 299 (1974).
 - (8) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, **91**, 1346 (1969).
 - (9) P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. 1, Academic Press, New York, N.Y., 1974, pp 329 and 420.
 - (10) (a) J. J. Bishop and A. Davison, *Inorg. Chem.*, **10**, 832 (1971); (b) C. G. Pierpont and R. Eisenberg, *ibid.*, **11**, 828 (1972); (c) M. Pankowski, B. Demerseman, G. Bouquet, and M. Bigorgne, *J. Organomet. Chem.*, **35**, 155 (1972); (d) M. Pankowski and M. Bigorgne, *ibid.*, **35**, 397 (1972).
 - (11) (a) L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 6974 (1965); (b) L. Malatesta, M. Angoletta, and G. Caglio, *J. Chem. Soc. A*, 1836 (1970).
 - (12) T. Kruck and M. Noak, *Chem. Ber.*, **97**, 1693 (1964).
 - (13) W. Hieber and V. Frey, *Chem. Ber.*, **99**, 2614 (1966).
 - (14) (a) W. J. Cherwinski and H. C. Clark, *Can. J. Chem.*, **47**, 2665 (1969); (b) H. Kurosawa and R. Okawara, *J. Organomet. Chem.*, **71**, C35 (1974).
 - (15) M. Hidai, M. Kokura, and Y. Uchida, *J. Organomet. Chem.*, **52**, 431 (1973).
 - (16) When this reaction was performed in the absence of carbon monoxide or in boiling methanol, two kinds of nickel complexes, [C₆Cl₅Ni-(PPhMe₂)OCH₃]₂ (mp 171 dec °C) and [C₆Cl₅Ni(PPhMe₂)₃]⁺ClO₄⁻ (**8**), were obtained.
 - (17) J. E. Byrd and J. Halpern, *J. Am. Chem. Soc.*, **93**, 1634 (1971).
 - (18) D. M. Barlex and R. D. W. Kemmitt, *J. Chem. Soc., Dalton Trans.*, 1436 (1972).
 - (19) S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, and K. Ataka, *J. Am. Chem. Soc.*, **95**, 3180 (1973).
 - (20) (a) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961); (b) A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965); (c) L. E. Moore, R. B. Gayhart, and W. E. Bull, *J. Inorg. Nucl. Chem.*, **27**, 1341 (1965).
 - (21) M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, **11**, 1269 (1972).
 - (22) Reference 9, pp 51-62.
 - (23) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
 - (24) R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, *J. Am. Chem. Soc.*, **92**, 1511 (1970).
 - (25) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, Oxford, 1962, p 109.
 - (26) R. Uson, J. Fornies, and F. Martinez, *J. Organomet. Chem.*, **112**, 105 (1976).

Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

The Kinetics of Olefin-Olefin Substitution Reactions in a Series of Platinum(II) Complexes

STEPHEN S. HUPP*¹ and GEORGE DAHLGREN

Received January 19, 1976

AIC60049N

The kinetics of substitution of styrene by 1-pentene in a series of *trans*-PtCl₂(Ol)(An) complexes where An is a para-substituted aniline were studied in chloroform by stopped-flow methods. The second-order rate constants for substitution at 25 °C were found to be greater than 3000 M⁻¹ s⁻¹. The presence of small quantities of ethanol in the chloroform decreases the rates of the direct second-order substitution pathway and increases the apparent solvent-assisted pathway. The reactions in the reverse direction were complicated by the fast reaction with excess styrene to produce *trans*-dichlorobis(styrene)platinum. A kinetic trans effect was observed in the reactions in both directions, the rates of olefin substitution decreasing as a function of the para substituent on the aniline in the order Cl > H > CH₃ > OCH₃.

Introduction

The kinetics of ligand substitution reactions in square-planar platinum(II) complexes have been extensively studied.²⁻⁷ Nearly all of the substitution kinetics have been found to obey a two-term rate law describing two simultaneous reaction pathways. The k_1 term is the second-order rate constant for



$$\text{rate} = [k_1(\text{Y}) + k_s](\text{Pt}-\text{X}) \quad (2)$$

the direct bimolecular substitution of the leaving ligand (X) by the incoming ligand (Y). This path is generally believed to go through a five-coordinate, approximately trigonal-bipyramidal transition state, with the entering ligand (Y), the leaving ligand (X), and the trans ligand (T) in the trigonal plane. The k_s term represents a solvent assisted path, the rate of which is independent of the concentration of the entering ligand (Y). This path presumably involves the displacement of the leaving ligand by a solvent molecule in the rate-determining step by bimolecular substitution. The solvent molecule is then rapidly displaced by the incoming ligand to give the product complex.

The reactions are invariably carried out in a large excess of incoming ligand (Y) so that the data may be treated in a

first-order fashion to obtain the observed pseudo-first-order rate constant, eq 3. A plot of k_{obsd} vs. the concentration of

$$k_{\text{obsd}} = k_1(\text{Y}) + k_s \quad (3)$$

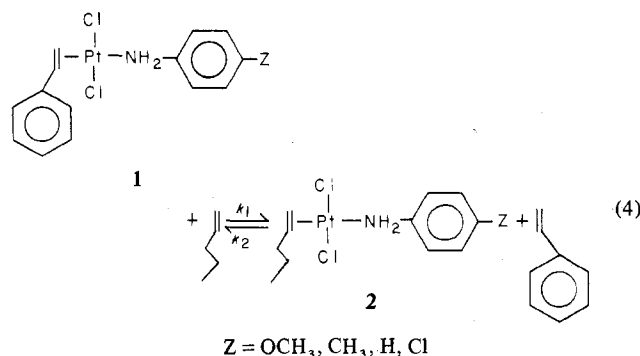
Y gives k_1 as the slope and k_s as the intercept.

In solvents which are capable of coordinating strongly to the metal the k_s term is usually found to make a significant contribution to the rate of reaction, sometimes dominating the direct path. In weakly coordinating solvents the solvent path makes little contribution, often indistinguishable from zero.

In 1936 Anderson first reported the substitution reactions of olefins in Zeise's salt and related compounds.⁸ These reactions have been widely used in the preparation of platinum-olefin compounds and the reactions are known to be fast. However, very little quantitative work has been done on the rates of olefin substitution in platinum(II) complexes.⁹⁻¹¹

In this work the rates of olefin-olefin substitution were studied by stopped-flow methods in a series of square-planar platinum(II) complexes of the type *trans*-PtCl₂(Ol)(An), where Ol is styrene or 1-pentene and An is a para-substituted aniline, eq 4.

Anilines were chosen as the trans ligands not only because of their ready availability but also because the para substituents markedly change the base strength of the primary amine group coordinated to the metal and it was anticipated that such a change in the σ donor properties of the amine should affect



to some extent the rates of olefin substitution in reaction 4 (the kinetic trans effect). At the same time, the para substituents are far removed from the reaction site and should exhibit minimal, if any, steric effects.

Experimental Section

Reagents and Solvents. 1-Pentene (Phillips Petroleum Co., pure grade, 99 mol % minimum; Chemical Samples Co., 99%) and styrene (Aldrich Chemical Co., 99%, *tert*-butylcatechol stabilizer) were used in the preparation and reactions of Pt complexes without further purification.

p-Anisidine (Matheson Coleman and Bell, reagent grade) was recrystallized from distilled water using decolorizing carbon (Fisher Norit-A) to help remove impurities.

p-Toluidine (Matheson Coleman and Bell, practical grade) was purified by being dissolved in about 2% HCl in the presence of decolorizing carbon, filtered, and precipitated from solution by addition of 10% NaOH.

Aniline (J.T. Baker, reagent grade) was purified by vacuum distillation.

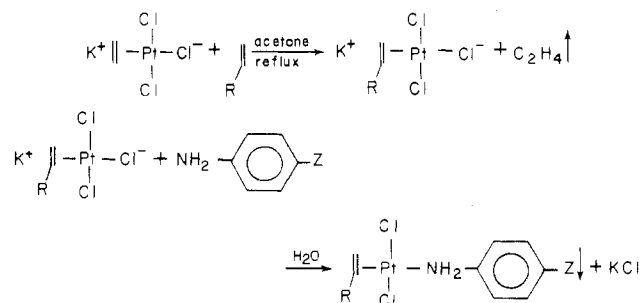
p-Chloroaniline (Eastman Organic Chemicals, reagent grade) was recrystallized from toluene and washed with cyclohexane.

The reagent grade chloroform used throughout this study (Fisher Scientific Co., Certified ACS reagent grade) contained about 0.75% ethanol as a preservative (ca. 0.13 M). The chloroform used as a solvent for kinetics and spectra was extracted twice with an equal volume of distilled water, dried over CaCl₂, and distilled from CaSO₄ (bp 61.0 °C). It was estimated by GC analysis that this procedure removed greater than 98% of the ethanol, leaving the concentration at less than 0.003 M ethanol. Hereafter we shall refer to this treated chloroform as pure chloroform. The chloroform used for equilibrium measurements was passed through a 1 in. × 7 in. column containing about 90 g of Woelm grade I neutral alumina at a flow rate of 2–4 ml/min. It was estimated by GC analysis that the column removed variously between 50 and 99% of the preservative ethanol. The chloroform used for absorbance and equilibrium measurements of μ -dichloro-(2,4-dichloro-1,3-styrene)diplatinum was extracted once with distilled water and passed through a column of neutral alumina as above. It was estimated that this procedure removed about 99% of the ethanol.

Matheson, Coleman, and Bell spectroquality chloroform was found to be unsuitable as a solvent in this study, since the stabilizer is an olefin which reacts with the Pt complexes.

***trans*-PtCl₂(O)(An).** All complexes of the type *trans*-PtCl₂(O)(An) were prepared by one of two general reaction sequences (Schemes I and II) each starting with Zeise's salt.

Scheme I



Scheme II

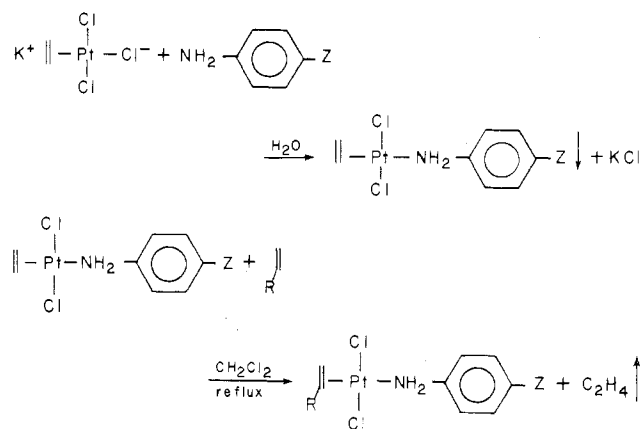


Table I. Melting Points and Elemental Analyses for *trans*-PtCl₂(RCH=CH₂)(*p*-NH₂C₆H₄Z) Complexes

R	Z	Mp, °C	Anal.			
			Calcd, %		Found, %	
			C	H	C	H
C ₃ H ₇	OCH ₃	86	31.38	4.17	31.08	4.20
C ₃ H ₇	CH ₃	85	32.51	4.32	32.65	4.38
C ₃ H ₇	H	102	30.78	3.99	30.73	3.74
C ₃ H ₇	Cl	84	28.49	3.48	28.63	3.45
Ph	OCH ₃	139	36.52	3.47	36.70	3.39
Ph	CH ₃	164	37.75	3.59	37.59	3.53
Ph	H	159	36.30	3.26	35.92	3.16
Ph	Cl	156	33.78	2.83	33.71	2.65

Sequence 1 (see Scheme I). Zeise's salt was dissolved in acetone and filtered through a fritted glass funnel to remove undissolved KCl. An excess of olefin was added and the solution refluxed to drive off liberated ethylene. The Zeise's salt analogue was collected by evaporating the solution in a Buchi Rotovapor and dried in vacuo.

Equimolar quantities of the Zeise's analogue and the substituted aniline were dissolved in distilled water and the aniline solution was added dropwise with stirring to the solution of the Pt salt. The *trans*-PtCl₂(O)(An) product, which is insoluble in water, precipitated from solution, was collected by filtration, washed with distilled water, and dried in vacuo.

Sequence 2 (see Scheme II). Equimolar quantities of Zeise's salt and aniline were dissolved in distilled water and the aniline solution was added dropwise with stirring to the solution of Zeise's salt. The neutral complex *trans*-PtCl₂(ethylene)(An) precipitated from solution was collected by filtration, washed with water, and dried in vacuo.

The *trans*-PtCl₂(ethylene)(An) was dissolved in CH₂Cl₂, an excess of olefin was added, and the solution was refluxed to drive off liberated ethylene. If all went well, the product could be crystallized by the addition of excess cyclohexane. The product was collected, washed with cyclohexane, and dried in vacuo.

The new compounds prepared are characterized in Table I.

μ -Dichloro-(2,4-dichloro-1,3-styrene)diplatinum(II) was prepared by the method of Joy¹² except that the product was not further recrystallized after crystallization from the benzene reaction solution, mp 204 °C. The large difference between the mp of 169–171 °C reported by Joy and that found here is unexplained. Anal. Calcd for C₁₆H₁₆Pt₂Cl₄: C, 25.96; H, 2.18; Cl, 19.15. Found: C, 25.72; H, 2.16; Cl, 19.23.

Apparatus. Melting points were recorded on a Perkin-Elmer DSC-1B differential scanning calorimeter. Ultraviolet absorption spectra were recorded on a Cary 14 spectrophotometer.

The kinetics of reactions were followed by measuring the change in absorbance at 325 nm as a function of time using a Durrum-Gibson D-110 stopped-flow spectrophotometer equipped with a Durrum D-131 photometric log amplifier and interfaced with a Systems Data Inc. MAC-16 computer. A Teflon flow cuvette with a 20 mm path length was used for all kinetic measurements. All kinetic runs were recorded with a time constant setting of 0.1 ms in the log amplifier. The MAC-16 computer was used as an analogue to the digital converter and data recording device, sampling the analogue absorbance signal

Table II. Mean Values of Equilibrium Constants for Reaction 4 in the Reverse Direction

Z	K	Z	K
OCH ₃	0.0217 ± 0.0014	H	0.0206 ± 0.0005
CH ₃	0.0283 ± 0.0027	Cl	0.0213 ± 0.0008

at a data rate set on the associated clock and writing an array of hexadecimal coded absorbance values on magnetic tape. Kinetic data were read from the magnetic tape and processed using an IBM-370 computer.

Ultraviolet Absorption Spectra. The ultraviolet absorption spectra of complexes **1** and **2** were recorded in pure chloroform and reagent chloroform and Beer's law plots were calculated at various wavelengths. The complexes were found to obey Beer's law at all wavelengths and the spectrum of each complex was the same within experimental error in pure and reagent chloroform.

Kinetic Calculations. A total of 2048 points were collected and written on magnetic tape by the MAC-16 computer for each individual kinetic run. The data collection rate was selected so that most of the reaction was completed during the collection of the first 500 data points. When the data were processed on the IBM-370, the first 2000 points were read from the tape record and the absorbance-time array was reconstructed. The value for absorbance at infinite time (A_{∞}) was estimated by averaging the last 100 data points (after about 15–20 half-lives). In all but the fastest reactions a set of about 300–500 points was used in calculating the observed rate constant for each individual run. The minimum number used in processing any single run was about 70 points.

The observed rate constant for each run was calculated by fitting absorbance vs. time using a nonlinear least-squares program with an exponential function derived from the kinetic rate law.

Several kinetic runs were made with each set of reactant solutions. The weighted mean k_{obsd} and the standard deviation of the mean were calculated, taking the weight for each determination to be the squared inverse of its standard deviation. Second-order rate constants were obtained by a weighted linear least-squares calculation of mean k_{obsd} vs. concentration of entering olefin. The weight for each point was taken to be the squared inverse standard deviation of the mean k_{obsd} .

Equilibrium Calculations. The ultraviolet spectra of equilibrium solutions were recorded and the absorbances of the solutions were read from the spectra at various wavelengths. The equilibrium constant was calculated at each wavelength by fitting the measured absorbances vs. the initial concentrations of reactants using a nonlinear least-squares program with a function derived from the equilibrium constant expression. The adjustable parameters in the least-squares calculation were the equilibrium constant and the molar extinction coefficients of the absorbing species. Unless otherwise noted, the extinction coefficient of each species was obtained directly by a Beer's law plot and was input and held fixed in the calculation.

The value reported as the equilibrium constant for each reaction is the weighted mean of the values calculated at different wavelengths. The standard deviation of the weighted mean is also reported, although it may be a poor indication of the uncertainty in the value of the equilibrium constant.

Results and Discussion

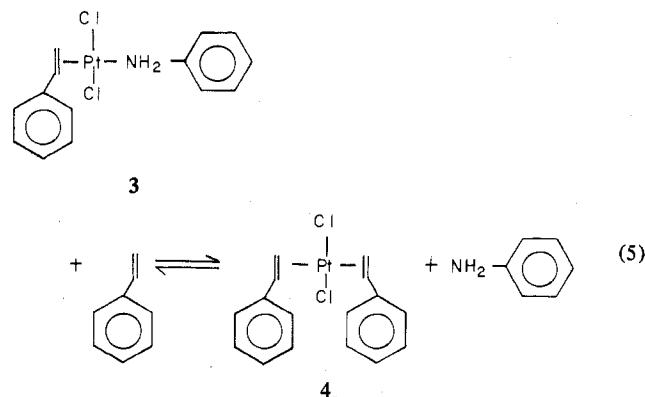
Equilibrium Studies. The equilibria of the series of reactions **4** were studied in the reverse direction by reacting styrene with the 1-pentene complexes. The equilibrium constants were calculated and the results are shown in Table II. However, significant systematic errors were observed in the calculations and further study of the aniline system revealed that at high styrene concentrations the measured absorbance throughout the spectrum between 320 and 380 nm was greater than that predicted for total conversion of the 1-pentene complex to the more highly absorbing styrene complex.

Spectra were recorded of *trans*-dichloro(styrene)(aniline)platinum, **3**, in the presence of increasing amounts of excess styrene. Not only was there an increase in absorbance throughout the spectrum with increasing styrene concentration, but a new peak appeared between about 360 nm and 380 nm, indicating the formation of a new species. When aniline was added to a solution of **3** containing excess styrene, the spectrum

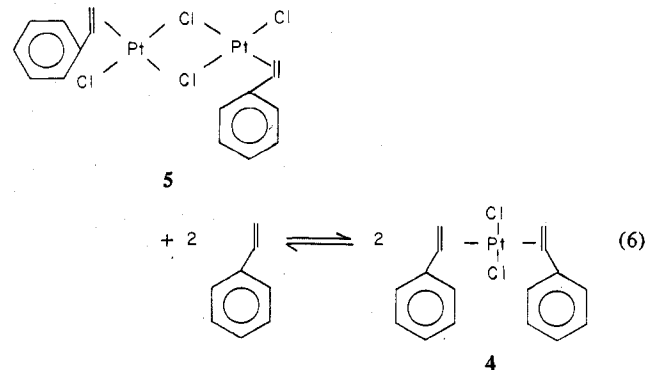
Table III. Equilibrium Constant for Reaction 6 and Molar Extinction Coefficients of **4** Calculated at Various Wavelengths

Wavelength, nm	K, M ⁻¹	ϵ_4 , M ⁻¹ cm ⁻¹
320	0.0242 ± 0.0020	11 100 ± 60
325	0.0249 ± 0.0020	11 070 ± 60
330	0.0238 ± 0.0024	11 190 ± 100
340	0.0229 ± 0.0018	12 160 ± 100
350	0.0232 ± 0.0021	12 990 ± 140
360	0.0234 ± 0.0015	13 360 ± 110
370	0.0227 ± 0.0020	12 870 ± 150
380	0.0227 ± 0.0022	10 030 ± 130

reverted to that predicted for **3**. We infer that the new species is *trans*-dichlorobis(styrene)platinum (**4**) formed by reaction **5**.



Further evidence for the formation of **4** in solution was obtained by reacting μ -dichloro-(2,4-dichloro-1,3-styrene)-diplatinum(II) (**5**) with styrene, reaction **6**. Ultraviolet spectra



of **5** in the presence of increasing amounts of styrene showed the expected new peak around 370 nm. The deep red color observed in these solutions is consistent with the observations of Anderson who assumed he had obtained impure **4** by the same reaction.⁸

Although the spectrum of **4** could not be measured directly in solution, the equilibrium constant of reaction **6** was calculated by adjusting both the equilibrium constant and the molar extinction coefficient of **4** in the nonlinear least-squares fitting of absorbance data at various wavelengths. Table III shows the results of the calculations. A weighted mean value of $0.0235 \pm 0.0003 \text{ M}^{-1}$ was found for the equilibrium constant of reaction **6**.

Using the calculated extinction coefficients for **4** the equilibrium constant for reaction **5** was calculated at various wavelengths. A weighted mean value of $3.38 \times 10^{-7} \pm 0.04 \times 10^{-7}$ was obtained.

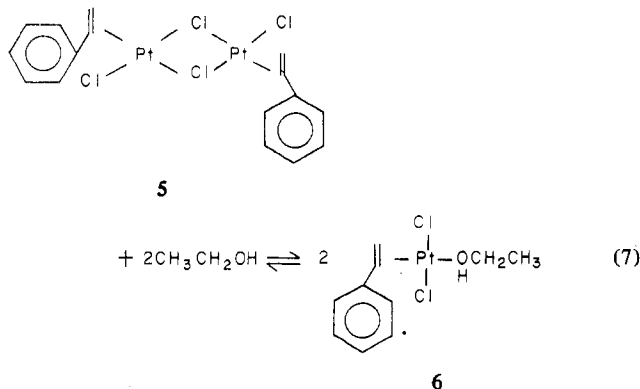
By analogy with reaction **5** an attempt was made to detect the formation of *trans*-dichlorobis(1-pentene)platinum by recording the spectra of *trans*-dichloro(1-pentene)(aniline)platinum in the presence of various amounts of 1-pentene.

Table IV. Rate Constants for Reaction 4 in the Forward Direction in Pure Chloroform at 25.0 °C

Z	$k_1, M^{-1} s^{-1}$	Intercept, s^{-1}	R
OCH ₃	3959 ± 10	-0.43 ± 0.13	0.999 986
CH ₃	5004 ± 24	0.02 ± 0.3	0.999 94
H	7030 ± 60	0.1 ± 0.7	0.999 8
Cl	9750 ± 80	1.8 ± 0.7	0.999 8

There was an overall small increase in absorbance in the presence of 1-pentene, but no new peaks appeared and a similar increase in absorbance was produced by the addition of hexane. It was concluded that the bis(1-pentene) complex could not be detected under the conditions of these experiments.

It was also found that ethanol reacts with **5**, probably cleaving the dimer as in reaction 7.¹³ Although the spectrum



of **6** appears to change with increasing ethanol and gives rise to systematic errors in the calculation, the equilibrium constant of reaction 7 was calculated by adjusting the equilibrium constant and the molar extinction coefficient of **6** in the nonlinear least-squares calculations. A weighted mean value of $0.0110 \pm 0.0007 M^{-1}$ was obtained.

Reaction Kinetics. The kinetics of reaction 4 in the forward direction were studied in pure chloroform and in reagent chloroform. The reactions were run using a large excess of 1-pentene and the kinetic data were treated first order to obtain the observed pseudo-first-order rate constants (eq 3). Such treatment of the data requires making two assumptions. The first is the common assumption that the concentration of the excess reactant (1-pentene) does not change during the course of the reaction. Since the smallest excess of 1-pentene used in this study was about 26 times the concentration of the Pt complex, the maximum error in any k_{obsd} which should arise from this assumption is less than 4%. The second assumption is that the reverse reaction may be neglected. Although the reactions are reversible, the equilibria favor formation of the 1-pentene complexes and, in excess 1-pentene, the reactions go essentially to completion (in all cases greater than 99%).

The function used in fitting the data is shown in eq 8. The

$$A_t = A_\infty + (A_0 - A_\infty)e^{-k_{\text{obsd}}(t+\theta)} \quad (8)$$

parameter A_0 was fixed at a value calculated from the molar extinction coefficient of the reactant complex and A_∞ was fixed at the value found by averaging the last 100 data points. The parameters k_{obsd} and θ were adjusted to give the best fit to the data.

Tables IV and V summarize the results of plots of k_{obsd} vs. [1-pentene]. The second-order rate constants obtained in reagent chloroform are about 14–20% smaller and the intercepts are substantially larger than those obtained in pure chloroform. The reactions were also carried out in reagent chloroform which had been passed through a column of neutral alumina and contained an amount of ethanol intermediate between the pure and original reagent chloroform. In each

Table V. Rate Constants for Reaction 4 in the Forward Direction in Reagent Chloroform at 25.0 °C

Z	$k_1, M^{-1} s^{-1}$	Intercept, s^{-1}	R
OCH ₃	3340 ± 13	1.96 ± 0.16	0.999 96
CH ₃	4270 ± 40	4.4 ± 0.5	0.999 8
H	6010 ± 50	12.1 ± 0.5	0.999 8
Cl	7800 ± 150	29.3 ± 1.3	0.998 8

case the slope and intercept obtained were between the values found in pure and untreated reagent chloroform.

The simplest interpretation of the results is consistent with that normally invoked to describe substitution reactions in platinum(II) complexes (eq 1 and 2). Since chloroform is noncoordinating, or at most very weakly coordinating, a solvent pathway in which chloroform displaces the leaving group and occupies a coordination site is not expected to make a large contribution to the rates of the reactions. Indeed, the intercepts obtained in pure chloroform are all within about three standard deviations of zero. However, there is a trend in the intercepts which parallels that obtained in reagent chloroform. This trend probably arises from a combination of two effects. First, in the pure chloroform the remaining trace of ethanol is still in excess of the total concentration of platinum. Second, the assumptions made in treating the data are approximations and would be expected to give rise to just such small systematic errors.

Since ethanol is strongly coordinating, the substantial nonzero intercepts obtained in reagent chloroform and the dependence of the intercepts on the amount of ethanol present are consistent with a solvent pathway in which ethanol may displace the leaving group (styrene) and is in turn displaced by the entering group (1-pentene).

Another possible interpretation involves displacement of the aniline by ethanol in the rate-determining step followed by a rapid sequence of substitutions leading to the product complex. The attractive feature of this route rests on the observation that in substitution reactions of $PtCl_2(\text{olefin})(\text{ligand})$ complexes, olefins most readily replace olefins and purely σ bonding ligands most readily replace their counterparts.¹⁴

The decrease in the second-order rate constants in the presence of ethanol is interpreted as indicating stronger solvation of the reactant complexes by ethanol than by chloroform. Although the concentration of ethanol in reagent chloroform is small, it was about 500 times the concentration of the platinum complexes. Such solvation by ethanol might be by a stronger general solvation sphere around the complexes or a specific solvation by ethanol occupying more or less strongly a fifth coordination site in the coordinatively unsaturated complexes. The former would require rearrangement of the coordination sphere and the latter would require displacement of ethanol from the complexes in going to the trigonal-bipyramidal transition state. Either case should impede attack by 1-pentene and stabilize the ground state relative to the transition state, thereby decreasing the rates of the direct substitution pathway in the presence of ethanol.

Although the decrease in rates might also be ascribed to a medium effect, the reaction involves all neutral species, and such a decrease in rates would seem large for the small change in the physical properties of the medium upon addition of less than 1% ethanol.

The kinetics of reaction 4 in the reverse direction were studied in pure chloroform. The reactions were run using a large excess of styrene and again the assumption was made that the concentration of the excess olefin was constant during the course of a reaction. In this direction, however, the reactions do not go to completion and the opposing reactions cannot be neglected. The data were treated first-order forward, second-order reverse using eq 9, where $q = b^2 - 4ac$; $a = k_{\text{obsd}}C_0$; $b = -k_{\text{obsd}}$; $c = -k_r$; C_0 = initial concentration of **2**;

$$A_t = A_0$$

$$+ (A_\infty - A_0) \frac{e^{q^{1/2}(t+\theta)} - 1}{e^{q^{1/2}(t+\theta)} - [(b + q^{1/2})/(b - q^{1/2})]} \quad (9)$$

k_{obsd} = observed pseudo-first-order rate constant in the direction run; and k_r = second-order rate constant in the opposite direction. The second-order rate constants for the opposing reactions were fixed at the values obtained for reaction 4 in the forward direction in pure chloroform. In each case the parameter θ was fixed at zero. Good nonlinear least-squares fits were obtained by adjusting the parameters k_{obsd} , A_0 , and A_∞ , although this treatment of the data is an approximation and there were systematic deviations from the initial estimates in the fitted values of A_0 and A_∞ . Table VI shows the results of plots of k_{obsd} vs. [styrene].

Table VI. Apparent Rate Constants for Reaction 4 in the Reverse Direction in Pure Chloroform at 25.0 °C

Z	$k_2, \text{M}^{-1} \text{s}^{-1}$	Intercept, s^{-1}	R
OCH ₃	116 ± 1	0.43 ± 0.03	0.999 988
CH ₃	167 ± 3	0.86 ± 0.09	0.999 5
H	303 ± 4	2.36 ± 0.20	0.999 7
Cl	512 ± 6	3.36 ± 0.10	0.999 7

Throughout this treatment the subsequent reaction of the product styrene complex with styrene to produce 4 was neglected. This was made necessary by the fact that the information needed to take account of the subsequent reaction could not be obtained. An attempt was made to observe reaction 5 in the Durrum stopped-flow spectrophotometer, but the reaction was so fast and the absorbance change so small that no reaction could be observed. Even treating the subsequent reaction as a very fast equilibrium would dictate a very complicated rate law and would likely be a bad approximation. Thus the second-order rate constants are reported in Table VI as "apparent" second-order rate constants and no conclusions can be drawn about the mechanism of reaction 4 in the reverse direction. The best that can be said is that the rates of reaction 4 in the reverse direction follow the same trend as in the forward direction with respect to the para substituent on the aniline. The rates of reaction in both directions decrease in the order Cl > H > CH₃ > OCH₃.

Table VII summarizes the trans effect as observed in reaction 4 in the forward direction in pure chloroform. The rate of olefin substitution decreases with increasing base strength of the aniline trans to the olefins. A weighted linear least-squares calculation of log (k_1) vs. the Hammett substituent constant (σ) gives a slope (ρ) of 0.82 ± 0.006 and a correlation coefficient of 0.995.

Although it is tempting to analyze the systematic electronic effects of substituents on the aniline in terms of σ and π influences on the relative stabilities of ground and transition states of the complexes, we believe insufficient data are available to sort out these effects with confidence. According to the σ trans effect theory,^{2,3} it would be anticipated that the rates of reaction would increase in going from the least basic aniline (*p*-chloroaniline) to the most basic aniline (*p*-anisidine), which is contrary to the results found here. This is not to say

Table VII. Comparison of the Rate Constants for Reaction 4 in the Forward Direction in Pure Chloroform with Parameters Characteristic of the Aniline Trans to the Olefin

Z	$k_1, \text{M}^{-1} \text{s}^{-1}$	σ^a	ρK_a^b
Cl	9750	0.227	4.15
H	7030	0.0	4.63
CH ₃	5004	-0.170	5.08
OCH ₃	3959	-0.268	5.34

^a Hammett substituent constant. Reference 15. ^b Reference 16.

that such an effect is not operable in this system, rather it must be overridden by some other effect or combination of effects. Assuming an increasing electron density on platinum in going from the least basic aniline to the most basic aniline, arguments might be invoked in terms of increased electron pair repulsions in the transition state, destabilizing the transition state relative to the ground state,¹⁷ and an enhancement of the platinum-olefin π bond in the ground state to a greater extent than the σ bond is weakened,³ stabilizing the ground state relative to the transition state. We are inclined to believe that the major factor leading to the difference in rate constants is the greater ground state stabilization of the complex containing the aniline which is the strongest base. It is not surprising that such a ground state effect is not observed in the measured equilibrium constants, since a similar stabilization should be exhibited in both the 1-pentene and styrene complexes.

Acknowledgment. The authors wish to express their deepest appreciation to Dr. Milton Orchin for his invaluable assistance throughout the course of this research and to Dr. Edward Deutsch for many valuable discussions.

Registry No. *trans*-PtCl₂(C₃H₇CH=CH₂)(*p*-NH₂C₆H₄OCH₃), 59982-14-8; *trans*-PtCl₂(C₃H₇CH=CH₂)(*p*-NH₂C₆H₄CH₃), 59982-15-9; *trans*-PtCl₂(C₃H₇CH=CH₂)(NH₂C₆H₅), 59982-16-0; *trans*-PtCl₂(C₃H₇CH=CH₂)(*p*-NH₂C₆H₄Cl), 59982-17-1; *trans*-PtCl₂(PhCH=CH₂)(*p*-NH₂C₆H₄OCH₃), 59982-18-2; *trans*-PtCl₂(PhCH=CH₂)(*p*-NH₂C₆H₄CH₃), 59982-19-3; *trans*-PtCl₂(PhCH=CH₂)(NH₂C₆H₅), 59982-20-6; *trans*-PtCl₂(PhCH=CH₂)(*p*-NH₂C₆H₄Cl), 59982-21-7; 5, 60018-53-3; 4, 59982-22-8; Zeise's salt, 16405-35-9; styrene, 100-42-5; 1-pentene, 109-67-1.

References and Notes

- Address correspondence to this author at Gulf Research and Development Company, Pittsburgh, Pa., 15230.
- C. H. Langford and H. B. Gray, "Ligand Substitution Processes", W. A. Benjamin, New York, N.Y., 1965, Chapter 2.
- F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967, Chapter 5.
- D. S. Martin, Jr., *Inorg. Chim. Acta, Rev.*, **1**, 87 (1967).
- L. Cattalini, *Prog. Inorg. Chem.*, **13**, 263 (1970).
- L. Cattalini, *MTP Int. Rev. Sci., Inorg. Chem., Ser. One*, **1972**, 269 (1972).
- F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science Publishers, Ltd., London, 1973, Chapter 11.
- J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).
- K. Konya, J. Fujita, H. Kido, and K. Saito, *Bull. Chem. Soc. Jpn.*, **2161** (1972).
- R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).
- G. Paiaro and A. Panunzi, *Ric. Sci., Parte 2: Sez. A*, **601** (1964).
- J. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 304 (1959).
- D. G. McMane and D. S. Martin, Jr., *Inorg. Chem.*, **7**, 1169 (1968).
- S. I. Shupack and M. Orchin, *J. Am. Chem. Soc.*, **86**, 586 (1964).
- H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
- "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969, p D-115.
- L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).