Contribution from Istituto di Chimica Fisica,
Università di Messina, 98100 Messina, Italy

Substituent Effects on the Rates of Uncatalyzed Cis to Trans Isomerization and Methanol Solvolysis of Arylplatinum Complexes: Inferences on the Nature of the Aryl–Metal Bond

RAFFAELLO ROMEO,* DOMENICO MINNITI, and SANTO LANZA

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The complexes *cis*-[Pt(PEt$_3$)$_2$(YC$_6$H$_4$)X] (X = Cl, Br, I and Y = H; X = Cl and Y = H, *m*-Me, *p*-Me, *m*-OMe, *p*-OMe, *m*-F, *p*-F, *m*-Cl, *p*-Cl, *m*-CF$_3$, *p*-CF$_3$) spontaneously convert to their trans isomers in methanol, and for all systems the isomeric equilibrium lies well over to the trans form. Large values of enthalpy of activation and positive entropies of activation are associated with isomerization. The rates of isomerization (k_i, s^{-1}) suffer mass-law retardation by X and are sensitive either to the nature of the halide ion or to changes in the electron density at the metal, brought about by para and meta substituents on the aromatic ring. The same factors hardly affect the rates of solvolysis (k_1, s^{-1}) which are at least 10^3 times higher than k_i and are characterized by low enthalpies and largely negative entropies of activation. These findings confirm that uncatalyzed isomerization of *cis*-[Pt(PEt$_3$)$_2$(aryl)X] complexes involves as a rate-determining step the breaking of the Pt–X bond followed by the interconversion of two T-shaped three-coordinate (i.e., 14-electron) intermediates. Correlation of k_i with Hammett's parameters of the Y substituents or with the set of Swain and Lupton dual-substituent parameters indicates that σ rather than π interactions are dominant in the aryl–platinum bond.

Introduction

Reactions of square-planar complexes are overwhelmingly stereospecific, and it is generally assumed that (except for photochemical reactions) a catalyst is required to produce isomerization.[1] Catalyzed isomerizations have been the subject of extensive investigations from both thermodynamic and mechanistic viewpoints.[2] While there has been some controversy concerning the mechanism, it was generally found that for complexes of the type [ML$_2$X$_2$] (M = Pt^{II} or Pd^{II}; L = tertiary phosphine, arsine, or stibine) the presence of a catalyst, added or generated from the substrate, is a prerequisite for the occurrence of the geometrical interconversion.

By way of contrast, we found that complexes of the type *cis*-[Pt(PEt$_3$)$_2$(R)X] (R = aryl or alkyl; X = halide ions), even though inert in apolar solvents, undergo spontaneous isomerization to trans isomers in protic solvents. Detailed kinetic studies on some of these systems[3] led us to suggest that, notwithstanding the well-known propensity for the metal to form five-coordinate species either as discrete compounds or as reaction intermediates, a bimolecular solvolysis is not the initial step of the isomerization, as found in some case for more labile PdL$_2$X$_2$ complexes.[4] On the contrary the mechanism of isomerization involves as rate-determining step the breaking of the Pt–X bond followed by the interconversion of two geometrically distinct T-shaped three-coordinate intermediates. The most convincing evidence for the operation of a D mechanism was obtained by comparing strain effects produced by ortho substituents on the rates of solvolysis and isomerization.[3c]

Since changes of electron density at the metal produced by para and meta substituents on the aromatic ring can play an important role in governing the stability of the transition state leading to the 14-electron platinum cation intermediate, we have undertaken a systematic kinetic study of cis to trans isomerization and methanol solvolysis of *cis*-[Pt(PEt$_3$)$_2$(YC$_6$H$_4$)X], where the substituent Y encompasses a wide range of electron-donating ability. Besides confirming the dissociative mechanism, these results provide a means of ascertaining the relative importance of σ and π interactions in the aryl–metal bond.

Experimental Section

Materials. Benzene and diethyl ether were dried over sodium wire. Anhydrous methanol was obtained by distillation of the reagent grade solvent over Mg(OCH$_3$)$_2$. "Anhydrous" LiClO$_4$ (99.8%) was purchased from K&K Fine and Rare Chemicals. All the other reagents were used without further purification.

Preparation of Compounds. Most of the starting diaryl substrates *cis*-[Pt(PEt$_3$)$_2$(YC$_6$H$_4$)$_2$] were prepared by literature methods (Y = H,[5] *p*-OMe,[6] *m*-OMe,[8] *p*-Me,[5] *p*-F,[7] *m*-F,[7] *p*-Cl,[8] *p*-CF$_3$,[8] and *m*-CF$_3$[8]), and their analyses were satisfactory.

The following are new.

cis-**[Pt(PEt$_3$)$_2$(*m*-MeC$_6$H$_4$)$_2$].** *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] (1.0 g) suspended in dry benzene (25 mL) was reacted with 20 mL of an ethereal solution of *m*-MeC$_6$H$_4$Li (0.41 M, prepared from *m*-MeC$_6$H$_4$Br by halide–metal interchange with *n*-butyllithium[9]). The mixture was stirred at room temperature for 1 h and then hydrolyzed with ice. The crude product isolated from the organic layer by evaporation was crystallized as white plates (0.82 g) from petroleum ether (40–70 °C); mp 143–144 °C. Anal. Calcd: C, 50.90; H, 7.25. Found: C, 51.00; H, 7.40.

cis-**[Pt(PEt$_3$)$_2$(*m*-ClC$_6$H$_4$)$_2$].** This was prepared in an analogous way by reacting *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] (1.0 g) in dry benzene (25 mL) with *m*-ClC$_6$H$_4$Li[9] (0.81 mmol) in diethyl ether (15 mL). The crude product was chromatographed on alumina. Elution with petroleum ether (40–70 °C) containing ether (20%) gave the product as white needles (0.86 g) from *n*-heptane; mp 152–154 °C. Anal. Calcd: C, 44.05; H, 5.85. Found: C, 44,15; H, 5.80.

The preparation of most of the *cis*-[Pt(PEt$_3$)$_2$(YC$_6$H$_4$)Cl] complexes (Y = *m*-OMe, *p*-OMe, *p*-Cl, *m*-CF$_3$, *p*-CF$_3$) has been already reported.[8] The following new compounds (Y = *m*-Me and *m*-Cl) were prepared by using essentially the same procedure which involves the electrophilic attack of a stoichiometric quantity of dry HCl in diethyl ether on a weighed amount of the corresponding cis diaryl compound in dry benzene.

Anal. Calcd for *cis*-[Pt(PEt$_3$)$_2$(*m*-MeC$_6$H$_4$)Cl] (mp 122–125 °C), C$_{19}$H$_{37}$ClP$_2$Pt: C, 40.90; H, 6.70. Found: C, 41.09; H, 6.77. Calcd for *cis*-[Pt(PEt$_3$)$_2$(*m*-ClC$_6$H$_4$)Cl] (mp 142–145 °C), C$_{18}$H$_{34}$Cl$_2$P$_2$Pt: C, 37.40; H, 6.09. Found: C, 37.35; H, 5.84.

The other compounds where Y = H,[5] *p*-Me,[5], *m*-F,[7], and *p*-F[7] and the complex *cis*-[Pt(PEt$_3$)$_2$(C$_6$F$_5$)Cl][10] were prepared by the literature methods, and their analyses were satisfactory.

The best way for assigning a cis geometry to the [Pt(PEt$_3$)$_2$(YC$_6$H$_4$)X] complexes is to follow their spontaneous conversion to trans isomers in methanol. The stereochemistry of these compounds was also established through the number of bands observed in the 410–440 cm^{-1} region of the infrared spectra (measured on Nujol mulls with a Perkin-Elmer 577 spectrophotometer). The cis compounds showed two weak vibrations, ascribed to platinum–phosphorus stretching frequencies,[11] while only one medium band, centered at 413 ± 2 cm^{-1}, was exhibited by a series of trans derivatives (Y = H, *p*-OMe, *m*-OMe, *p*-Me, *m*-Me, *p*-F, *m*-F, *p*-CF$_3$). The Pt–Cl stretch for the cis compounds is centered at 280 ± 3 cm^{-1} whereas that for the trans isomers is found at the lower frequency 271 ± 3 cm^{-1}.

The ^{1}H NMR spectra were determined on an Hitachi Perkin-Elmer R24B spectrometer with CDCl$_3$ as the solvent and Me$_4$Si as internal reference. The methyl protons of the triethylphosphine ligand give two triplets partially overlapping for the cis isomers, whereas they appear as a very characteristic five-line pattern for the trans de-

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Table I. Temperature Dependence of the Rate of Cis to Trans Isomerization of $[Pt(PEt_3)_2(R)Cl]$ Complexes in Methanol

R	temp, °C	10^3k_i, s^{-1}	R	temp, °C	10^3k_i, s^{-1}	R	temp, °C	10^3k_i, s^{-1}
Ph	15	0.190	p-$OMeC_6H_4$	15	0.210	p-ClC_6H_4	25	0.06
	20	0.481		20	0.510		30	0.160
	25	1.21		25	1.48		35	0.360
	30	2.95		30	3.30		40	0.740
	35	5.98		35	7.10			
m-MeC_6H_4	15	0.374	m-FC_6H_4	25	0.0894	m-$CF_3C_6H_4$	25	0.029
	20	0.805		30	0.194		30	0.070
	25	1.95		35	0.520		35	0.153
	30	4.98		40	1.13		40	0.342
	35	10.2		45	2.40		45	0.720
p-MeC_6H_4	15	0.340	p-FC_6H_4	20	0.085	p-$CF_3C_6H_4$	25	0.043
	20	0.850		25	0.22		30	0.105
	25	2.02		30	0.44		35	0.232
	30	4.76		35	1.25		40	0.581
	35	10.0		40	2.56		45	1.28
m-$OMeC_6H_4$	15	0.113	m-ClC_6H_4	25	0.0578			
	20	0.305		30	0.144			
	25	0.805		35	0.355			
	30	2.07		40	0.858			
				45	1.663			

rivatives.[7,12] The number of protons, determined by integration, were in agreement with the assigned structures.

Kinetics

The isomerization reactions were followed spectrophotometrically by measuring spectral changes of the reaction mixture with time in the range 320–220 nm by means of an OPTICA CF 4 recording spectrophotometer and, at a fixed wavelength, by using a Beckman DU instrument equipped with a Saitron 301 photometer and a Servogor S recording potentiometer. The spectrophotometer cell served as the reaction vessel.

The reactions were started by adding a weighed amount of a finely powdered sample of the complex to a prethermostated volume of solvent in the thermostated (±0.1 °C) cell compartment of the spectrophotometer and shaking the solution rapidly.

The nucleophilic substitution reactions of *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ complexes with I^- were followed by means of a Durrum-Gibson D 110 stopped-flow spectrophotometer with a 20-mm observation cell. A Tektronics Model 564 storage oscilloscope equipped with a Polaroid camera was used to record the absorbance data. Isomerization of the starting complex was prevented by dissolving the substrate in 0.01 M lithium chloride. A large excess of reagent was used to provide pseudo-first-order conditions.

The pseudo-first-order rate constants of the isomerization (k_i, s^{-1}) and of the nucleophilic substitution (k_1, s^{-1}) were obtained from the gradients of plots of log ($A_t - A_\infty$) vs. time (A = optical density). Activation parameters were computed by a nonlinear regression analysis of a fit of experimentally observed rate constants to the Eyring equation.[13]

Results

In the absence of free phosphine as catalyst, the complexes *cis*-$[Pt(PEt_3)_2(R)X]$ are very stable in nonpolar solvents which are used currently for their synthesis and purification. On the contrary, the same species start to convert to trans isomers as soon as the solid compounds are dissolved in methanol. The spectra between 320 and 220 nm show well-defined isosbestic points, indicating that the two isomers are the only absorbing species in solution. In all cases the equilibria lie well over to the trans form; in each kinetic run the final spectrum of the reaction mixture was identical with that of an authentic sample of trans isomer. The same pattern of behavior is observed in a series of alcohols where the rate of isomerization is found to decrease with the decreasing of the charge-separating ability of the solvent.[14]

Table II. Effect of Lithium Chloride on the Rate of Cis–Trans Isomerization of the Complexes $[Pt(PEt_3)_2(R)Cl]$ in Methanol[a,b]

R	$10^4 \times [Cl^-]$, M	10^4k_i, s^{-1}	R	$10^4 \times [Cl^-]$, M	10^4k_i, s^{-1}
Ph[c]	0.0	48.4	m-FC_6H_4[c]	0.0	2.11
	1.0	15.4		1.0	0.72
	2.0	9.60		2.0	0.45
	4.0	5.22		3.0	0.32
	10.0	2.17	p-FC_6H_4[c]	0.0	5.15
	12.0	1.82		2.0	1.30
m-MeC_6H_4[c]	0.0	80.6		4.0	0.75
	2.0	15.0		6.0	0.51
	4.0	9.01	m-ClC_6H_4[d]	0.0	18.6
	7.0	5.13		1.0	7.48
	15.0	2.50		2.0	4.54
	20.0	1.90		4.0	2.99
p-MeC_6H_4[c]	0.0	88.8	p-ClC_6H_4[d]	0.0	14.4
	1.0	27.4		1.0	8.20
	2.0	16.4		2.0	6.71
	4.0	8.4		4.0	3.72
	10.0	3.42			
m-$MeOC_6H_4$[c]	0.0	32.3	m-$CF_3C_6H_4$[d]	0.0	13.4
	1.0	13.6		1.0	3.13
	2.0	7.62		2.0	1.68
	4.0	4.00	p-$CF_3C_6H_4$[d]	0.0	12.1
	8.0	2.24		1.0	3.90
	12.0	1.51		2.0	2.18
p-$MeOC_6H_4$[c]	0.0	43.5			
	1.0	15.6			
	2.0	11.5			
	4.0	6.00			
	10.0	2.40			
	12.0	2.10			

[a] [Complex] = 0.5×10^{-4} M. [b] μ = 0.01 M ($LiClO_4$). [c] At 30 °C. [d] At 45 °C.

The isomerization followed a first-order rate law. The specific rate constants at various temperatures are listed in Table I.

Although the nature of the observed changes remains the same, the rate of isomerization is greatly reduced by the addition of very small amounts of halide ion to the solution and approaches zero at higher concentrations. These kinetic runs were carried out by keeping the ionic strength constant at 0.01 M with $LiClO_4$. The first-order rate constants are listed in Table II and Table III. Plots of k_i^{-1} vs. $[X^-]$ are linear for all systems. The intercepts at $[X^-] = 0$ were identical with the k_i^{-1} values obtained in the absence of halide ion; however,

Table III. Effect of Varying [X^-] on the Rate of Cis to Trans Isomerization of [$Pt(PEt_3)_2(Ph)X$] Complexes in Methanol at 30 °C[a,b]

cis-[$Pt(PEt_3)_2(Ph)Cl$][c]	$10^4[Cl^-]$, M	0.0	1.0	2.0	4.0	10.0	12.0
	10^4k_i, s^{-1}	48.4	15.4	9.6	5.22	2.17	1.82
cis-[$Pt(PEt_3)_2(Ph)Br$][d]	$10^4[Br^-]$, M	0.0	0.8	2.0	4.0	8.0	12.0
	10^4k_i, s^{-1}	13.8	7.23	3.62	2.05	1.17	0.78
cis-[$Pt(PEt_3)_2(Ph)I$][e]	$10^4[I^-]$, M	0.0	1.0	1.5	2.0	3.0	
	10^4k_i, s^{-1}	6.07	0.52	0.35	0.25	0.18	

[a] [Complex] = 0.8×10^{-4} M. [b] $\mu = 0.01$ M ($LiClO_4$). [c] $k_{-D}/k_T = 2.40 \times 10^4$. [d] From ref 3c, $k_{-D}/k_T = 1.42 \times 10^4$. [e] $k_{-D}/k_T = 11.2 \times 10^4$.

Table IV. Temperature Dependence of the Rates of Chloride Displacement by MeOH from the Complexes *cis*-[$Pt(PEt_3)_2(R)Cl$][a]

R	temp, °C	k_1, s^{-1}	R	temp, °C	k_1, s^{-1}	R	temp, °C	k_1, s^{-1}
Ph	13	1.39	*p*-$MeOC_6H_4$	13	2.04	*p*-ClC_6H_4	13	1.38
	18	1.88		18	2.59		18	1.88
	30	3.33		30	5.29		30	3.32
	40	6.23		40	8.83		40	5.84
m-MeC_6H_4	15	1.49	*m*-FC_6H_4	13	1.30	*m*-$CF_3C_6H_4$	13	1.36
	22	2.03		20	1.90		18	1.69
	30	3.20		30	2.90		30	3.05
	40	6.03		37	4.80		40	5.65
p-MeC_6H_4	13	1.55	*p*-FC_6H_4	13	1.46	*p*-$CF_3C_6H_4$	13	1.45
	18	2.03		18	1.98		18	1.91
	30	3.90		30	3.60		30	3.07
	40	6.86		40	6.52		40	5.45
m-$MeOC_6H_4$	13	1.16	*m*-ClC_6H_4	15	1.48	C_6F_5	15	0.0042
	18	1.73		22	1.95		20	0.0068
	30	3.27		30	3.10		25	0.0093
	40	5.50		40	6.38		30	0.0132
							35	0.0174
							40	0.0233

[a] [Complex] = 0.2×10^{-4} M.

Table V. Effect of Varying [Cl^-] on the Rate of Chloride Substitution from *cis*-[$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$] by 0.1 M Iodide at 30 °C in MeOH

[Cl^-], M	k_{obsd}, s^{-1}	[Cl^-], M	k_{obsd}, s^{-1}
0.0	3.20	0.008	3.22
0.002	3.34	0.010	3.22
0.004	3.28	0.020	3.36

these values are still slightly different from that obtained in the neat solvent (compare Tables I and II at the same temperature) since the addition of inert salts to adjust the ionic strength increases the isomerization rate. The isomerization rates are also sensitive to the quantity of water present in the system so that careful drying of the solvent and of the materials is required to obtain good reproducibility.

In order to compare the relative magnitudes of the rates of isomerization (k_i, s^{-1}) and solvolysis (k_1, s^{-1}), we have examined the kinetics of nucleophilic substitution of chloride in *cis*-[$Pt(PEt_3)_2(R)Cl$] by iodide, which take place according to reaction 1. The reactions, carried out at various temperatures

$$cis\text{-}[Pt(PEt_3)_2(R)Cl] + I^- \rightarrow cis\text{-}[Pt(PEt_3)_2(R)I] + Cl^- \quad (1)$$

under pseudo-first-order conditions (excess of reagent), are virtually quantitative and occur at a rate independent of iodide concentration, obeying the rate law $-d[\text{complex}]/dt = k_1[\text{complex}]$. At variance with the usual behavior of platinum(II) complexes toward nucleophilic substitution, a second-order contribution is statistically insignificant in the 0.001–0.1 M I^- concentration range. Under these circumstances a very accurate measure of the k_1 values can be obtained as the mean for a number of runs carried out at different iodide concentrations. The k_1 values at different temperatures are listed in Table IV. Substitution of Cl^- in *cis*-[$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$] by 0.1 M I^- in the presence of an excess of added chloride (Table V) showed that k_1, unlike k_i, is not affected by large variations in chloride concentrations.

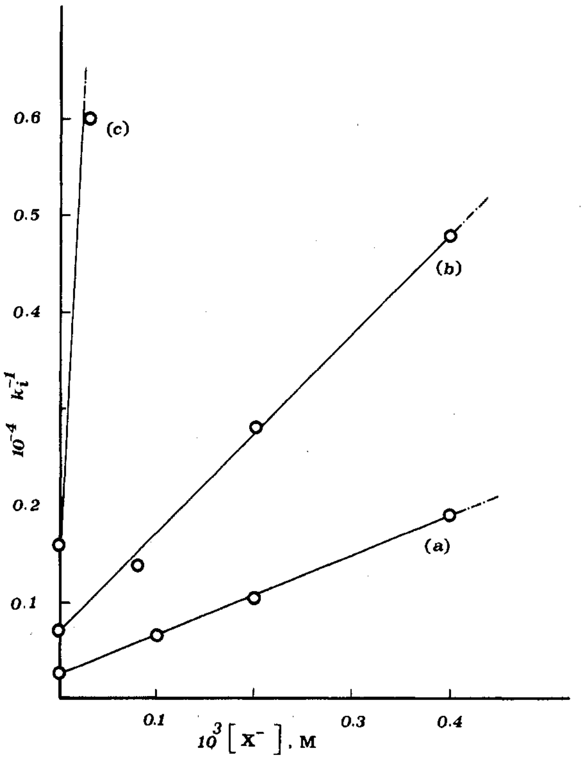


Figure 1. Effect of added X^- on the rate of cis–trans isomerization of *cis*-[$Pt(PEt_3)_2(Ph)X$] in methanol at 30 °C: (a) $X^- = Cl^-$, (b) $X^- = Br^-$, (c) $X^- = I^-$.

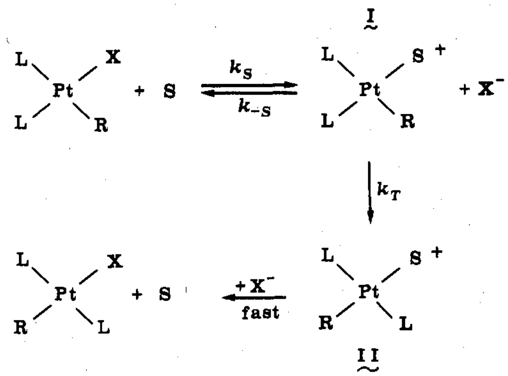
Discussion

Comparison of Mechanisms. Table II lists the kinetic data for the isomerization of *cis*-[$Pt(PEt_3)_2(R)Cl$] carried out in the presence of varying amounts of chloride ion added. On plotting the reciprocal of the k_i values for these experiments vs. chloride concentration, one obtains a straight line with a

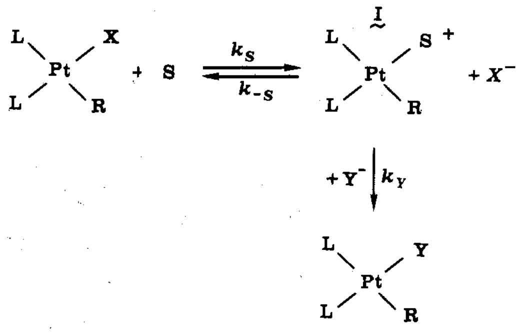
Table VI. Comparison of Rate Constants at 30 °C and Activation Parameters for Cis to Trans Isomerization (k_i, $\Delta H_i^{\ddagger}$, $\Delta S_i^{\ddagger}$) and Chloride Displacement by MeOH (k_1, $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$) for the Complexes *cis*-[Pt(PEt$_3$)$_2$(R)Cl]

R	$10^3 k_i$, s^{-1}	$10^{-4}(k_{-D}/k_T)$	$\Delta H_i^{\ddagger}$, kJ mol^{-1}	$\Delta S_i^{\ddagger}$, J K mol^{-1}	$10^3 k_1$, s^{-1}	$\Delta H_1^{\ddagger}$ kJ mol^{-1}	$\Delta S_1^{\ddagger}$, J K mol^{-1}
Ph	2.95	2.4	113 ± 4	+88 ± 12	3680	38.7 ± 0.1	−105 ± 0.2
m-MeC$_6$H$_4$	4.43	2.0	117 ± 4	+100 ± 17	3200	39.6 ± 2	−104 ± 8
p-MeC$_6$H$_4$	4.76	3.7	117 ± 2	+96 ± 8	3900	39.3 ± 1	−102 ± 4
m-MeOC$_6$H$_4$	2.07	1.9	138 ± 0.2	+162 ± 1	3270	38.5 ± 1	−107 ± 4
p-MeOC$_6$H$_4$	3.30	2.1	119 ± 3	+100 ± 8	5290	38.5 ± 1	−103 ± 3
m-FC$_6$H$_4$	0.194	1.8	124 ± 2	+92 ± 8	2900	39.3 ± 4	−104 ± 12
p-FC$_6$H$_4$	0.440	1.6	121 ± 4	+100 ± 21	3600	39.7 ± 2	−100 ± 8
m-ClC$_6$H$_4$	0.144	1.1	117 ± 4	+75 ± 17	3100	41.5 ± 4	−97 ± 20
p-ClC$_6$H$_4$	0.160	0.8	117 ± 4	+71 ± 12	3220	37.6 ± 2	−108 ± 4
m-CF$_3$C$_6$H$_4$	0.070	3.7	121 ± 1	+78 ± 3	3050	39.2 ± 3	−105 ± 8
p-CF$_3$C$_6$H$_4$	0.103	2.4	131 ± 3	+113 ± 8	3070	35.1 ± 3	−117 ± 8
C$_6$F$_5$					13	45.2 ± 1	−129 ± 4

Scheme I



Scheme II



finite intercept for all the examined systems. A similar pattern of behavior is shown by *cis*-[Pt(PEt$_3$)$_2$(Ph)Br] and *cis*-[Pt(PEt$_3$)$_2$(Ph)I] complexes (see Table III and Figure 1). These results indicate a rate law of the form

$$k_i = a/(b[X^-] + c) \qquad (2)$$

Since most of kinetic data reported to date for ligand catalyzed cis–trans isomerization of tertiary phosphine halide complexes [PtL$_2$X$_2$] are consistent with an associative consecutive displacement mechanism, and the dissociative mechanism is controversial,[15,16] we shall examine in detail all the mechanisms compatible with such a rate law.

The mechanism in Scheme I involves the reversible release of the halide ion during an associative attack by the solvent and the formation of a solvento intermediate I. In the k_T path this latter is converted to its trans counterpart II which eventually takes up X$^-$ to give the trans isomer. Taking into account that the isomeric equilibrium lies well over to the trans form and assuming that the reverse reaction can be neglected, a steady-state treatment of species I leads to the rate law

$$k_i = k_S k_T/(k_{-S}[X^-] + k_T) \qquad (3)$$

which has a form identical with eq 2.

In the absence of added halide ion, expression 3 simplifies to $k_i = k_S$, which means that the rate of unretarded isomerization is identical with that of the bimolecular solvolysis of the substrate. This latter can be easily determined from the ligand-independent path of the nucleophilic substitution. The solvento intermediate I is a common intermediate for either isomerization (Scheme I) or substitution (Scheme II). The rate law derived by applying a steady-state treatment to I is given in eq 4. Equation 4 reduces to $k_1 = k_S$ in the absence

$$k_1 = k_S k_Y[Y^-]/(k_{-S}[X^-] + k_Y[Y^-]) \qquad (4)$$

of added halide ion or when $k_Y[Y^-] \gg k_{-S}[X^-]$, as found for the substitution of Cl$^-$ in *cis*-[Pt(PEt$_3$)$_2$(*m*-MeC$_6$H$_4$)Cl] whose rates are not sensitive to the addition of varying amounts of Cl$^-$ (Table V). Mechanism I therefore requires that the rate constant for unretarded isomerization (k_i) have the same value as the rate constant for unretarded solvolysis (k_1), in sharp contrast to what is observed experimentally since k_1 is several orders of magnitude higher than k_i (see Table VI). On the basis of the above findings it is clear that the rate-determining step for the isomerization is not the initial solvolysis of the substrate.

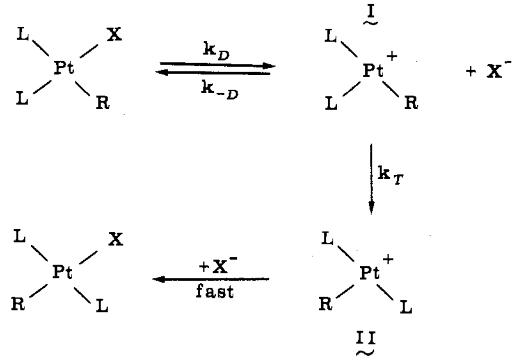
Mechanism 1 is essentially a mass-law retardation of isomerization of the solvento intermediate I by the leaving group X$^-$ and requires that the product of the rate constant for halide anation of I and the concentration of halide be comparable in magnitude to the rate constant for the isomerization of I. However, halide retardation can be very important also when solvolysis of *cis*-[Pt(PEt$_3$)$_2$(R)X] is fast and reversible and isomerization of the solvento species *cis*-[Pt(PEt$_3$)$_2$(R)S]$^+$ is relatively slow (k_S and $k_{-S} \gg k_T$). A preequilibrium treatment of Scheme I leads to the rate law given in eq 5, where $K_e = k_S/k_{-S}$. This rate expression (eq

$$k_i = k_T K_e/([X^-] + K_e) \qquad (5)$$

5) is still in agreement with eq 2 since it too predicts linear plots of k_i^{-1} vs. [X$^-$]. The intercept at [X$^-$] = 0 gives k_T^{-1}, namely, the reciprocal of the rate constant for the isomerization of the solvento intermediate, which obviously is independent of the nature of the leaving X$^-$. If a preequilibrium mechanism were operative, we would have expected that plots in Figure 1, which illustrate mass-law retardation of isomerization of *cis*-[Pt(PEt$_3$)$_2$(R)X] (X = Cl, Br, I), would not only be linear but also be all coincident in a unique intercept.

However, the unretarded isomerizations of *cis*-[Pt(PEt$_3$)$_2$(R)X] do not proceed at the same rate but decrease sharply in the order Cl$^-$ > Br$^-$ > I$^-$ with a reactivity ratio 1:0.28:0.12. Although this alone must rule out the preequilibrium mechanism, it is useful to add that if the substrate is partitioned between the halide and the reactive solvento species, at low enough [X$^-$] or when no halide is added, the latter species can be present in large amounts and should be

Scheme III



easily observable as a dependence of the initial spectrum on the concentration of halide ion. Such a dependence has not been observed under any circumstances when spectral scans were carried out at the low halide ion concentrations required.

A mechanism which accounts for all experimental findings is shown in Scheme III. Unlike Scheme I, this mechanism involves the dissociative loss of the X^- ligand and the conversion of two geometrically distinct T-shaped intermediates. Proceeding as for Scheme I and applying the steady-state approximation to I, one finds that the rate constant for isomerization is given by eq 6 which in the form of eq 7 accounts

$$k_i = k_D k_T/(k_{-D}[X^-] + k_T) \qquad (6)$$

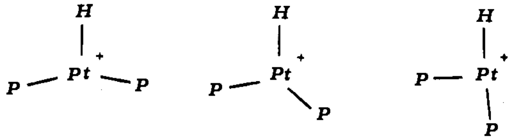
$$k_i^{-1} = k_D^{-1} + (k_{-D}/k_D k_T)[X^-] \qquad (7)$$

for linear plots of k_i^{-1} vs. $[X^-]$. When no X^- is added, eq 6 reduces to $k_i = k_D$, and hence the rate of metal–halide bond breaking, k_D, can be obtained either from the intercept of a mass-law retardation plot or, more simply, by carrying out the isomerization in the neat solvent.[17]

The suggested rate-determining bond cleavage in Scheme III receives strong support from the large values of enthalpy and entropy of activation associated with isomerization (see Table VI). To the best of our knowledge, the uncatalyzed isomerization of *cis*-$[Pt(PEt_3)_2(YC_6H_4)X]$ complexes is the only process to date in platinum(II) chemistry being characterized by largely positive entropies of activation. This reflects the greater freedom that the transition state possesses relative to the ground state. Accordingly, cis–trans isomerization is particularly sensitive to factors controlling bond dissociation: (i) electron-donating substituents on the aromatic ring enhance the rate of isomerization while electron-attracting groups have the reverse effect (see Table VI); (ii) the sequence of lability Cl > Br > I reflects the bond strength of the halide ions to the "soft" metal center. The low $\Delta H^{\ddagger}$ and largely negative $\Delta S^{\ddagger}$ values associated with the solvolysis agree with an associative mode of activation. Unlike isomerization, nucleophilic substitution is almost insensitive to substituent and leaving-group effects.

Very recently Kochi, Hoffmann, et al.[18] have proposed a dissociative mechanism strictly similar to that in Scheme III for cis–trans isomerization of the trialkyl(phosphine)gold complex *cis*-$[Et(CH_3)_2AuPPh_3]$. The T form which we have inferred for the coordinatively unsaturated $[RPtL_2]^+$ by means of competition experiments[3c] has been shown by molecular orbital calculations to be that of lower energy for a Me_3Au intermediate.[18] Thus three-coordinate ML_3 d^8 structures avoid the most symmetrical trigonal geometry in favor of T- and Y-shaped geometries of lower energy. T-shaped configurations are energy minima in the reaction profile for isomerization, and their interconversion occurs via a Y form. The same scheme holds for rearrangement of the less symmetrical $[HPt(PH_3)_2]^+$ species, although the energy barrier for conversion is very small (Scheme IV).[19] This molecular orbital study[19] also shows that the three-coordinate structure offers a favorable route for the insertion of ethylene into the Pt–H bond and supports views that the key intermediates in the insertion process as well as in the unassisted isomerization are three-coordinate and not four-coordinate.[20]

Scheme IV



Three-coordinate d^8 species (i.e., 14-electron compounds) are highly interesting not only from a structural viewpoint but also because of their relevant catalytic potential due to the site of coordinative unsaturation. While the number of processes in which the existence of three-coordinate intermediates is involved is growing in Pt^{II} chemistry,[2] their synthesis and isolation have been restricted to rhodium(I) compounds. Recently the three-coordinate Rh^I compounds $[RhX(PCy_3)_2]$[21] (X = F, Cl, Br, I; Cy = cyclohexyl), $[RhH(PCy_3)_2]$,[22] $[RhH(PBu_3)_2]$,[22] and $[Rh(PPh_3)_3]^+$[23] have been reported. An X-ray diffraction study of the $[Rh(PPh_3)_3]^+$ cation[23] showed a planar, approximately T-shaped, coordination of the three bulky ligands around the metal, the distortion away from sterically favored trigonal planarity being dictated by the need to allow diamagnetism.

Selectivity of the Three-Coordinate Intermediate. The ratio k_{-D}/k_T, which can be obtained from the slope of the mass-law retardation plot, measures the efficiency of X^- in capturing the three-coordinate intermediate I in competition with the isomerization process leading from I to II. Data in Table VI show that reassociation of the three-coordinate "cis-like" intermediate $[Pt(PEt_3)_2(YC_6H_4)]^+$ with Cl^- (1 M) is at least 10^4 times faster than its conversion to the "trans-like" counterpart. The ratio k_{-D}/k_T does not exhibit any particular trend along the series of complexes *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ and remains nearly constant, indicating that the nature of the Y substituent on the aromatic ring either does not influence or influences to the same degree the rates of halide reentry (k_{-D}) and isomerization (k_T).

The cis-like three-coordinate intermediate appears to have a lifetime long enough to discriminate among different nucleophiles. The ratios k_{-D}/k_T measured in the competition experiments for the complexes *cis*-$[Pt(PEt_3)_2(Ph)X]$ (X = Cl, Br, and I) (data in Table III) are 11.2×10^4 for I^-, 2.40×10^4 for Cl^-, and 1.42×10^4 for Br^-, respectively. The iodide ion is much more effective in capturing the transient intermediate "*cis*"-$[Pt(PEt_3)_2Ph]^+$ than Cl^- and Br^- which have comparable reactivity. A good deal more data for other entering groups are required to thoroughly test a sequence of nucleophilic reactivity toward the three-coordinate intermediate, but it is safe to anticipate that its nucleophilic discrimination ability appears similar to that of the corresponding tetracoordinates.

Meta- and Para-Substituent Effects. The rates of isomerization of the complexes *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ decrease with decreasing electron-donating ability of the Y substituent (see Table VI). The effect appears particularly relevant for *cis*-$[Pt(PEt_3)_2(C_6F_5)Cl]$ where strong inductive withdrawal of electron density from the metal by the perfluoroaryl group does not allow isomerization to take place even at high temperature. On the other hand, the rates of solvolysis are practically unaffected by changes in the nature of Y and remain almost constant along the series of complexes examined. The reduced reactivity of the pentafluorophenyl complex (10^2 times slower than the monosubstituted compounds) seems to be due mainly to steric strain by ortho fluoro substituents, although the strengthening of the Pt–Cl bond also

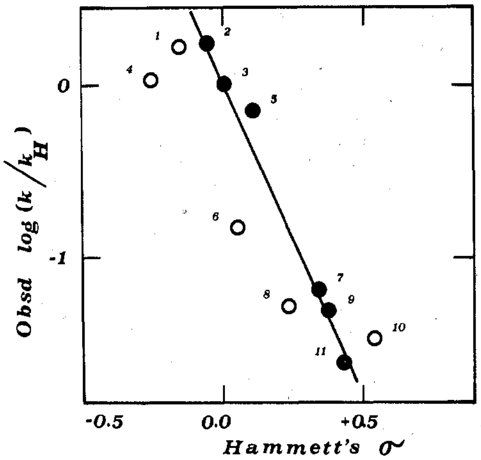


Figure 2. Hammett plot of para- and meta-substituent effects on the rate of cis–trans isomerization of $[Pt(PEt_3)_2(YC_6H_4)Cl]$ complexes in methanol at 30 °C: 1, *p*-Me; 2, *m*-Me; 3, H; 4, *p*-OMe; 5, *m*-OMe; 6, *p*-F; 7, *m*-F; 8, *p*-Cl; 9, *m*-Cl; 10, *p*-CF_3; 11, *m*-CF_3.

Table VII. Effect of Substituents on the Rate of Cis to Trans Isomerization of $[Pt(PEt_3)_2(YC_6H_4)Cl]$ Complexes at 30 °C

	substituent constant		log (k/k_H)			
			meta		para	
substituent	*F*	*R*	obsd	calcd	obsd	calcd
H	0.0	0.0	0.0	−0.024	0.0	−0.04
CH_3	−0.052	−0.141	0.227	0.284	0.207	0.281
OCH_3	0.413	−0.500	−0.150	−0.232	0.050	−0.036
F	0.708	−0.336	−1.182	−1.102	−0.827	−0.857
Cl	0.690	−0.161	−1.312	−1.305	−1.266	−1.100
CF_3	0.631	0.186	−1.625	−1.657	−1.449	−1.535

must be taken into account. The lack of an electronic cis effect parallels an analogous trans effect, since the complexes *trans*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ (Y = H,[24] *m*-F,[25] *p*-NO_2,[25] and *m*-CF_3[26]) were found to undergo nucleophilic substitution at comparable rates. These findings clearly indicate that the associative process is less sensitive and therefore less diagnostic than the dissociative one in revealing electronic interactions between metal and aryl ligands.

Figure 2 shows that the kinetic data for the isomerization as a whole give a rather random Hammett plot ($\log (k/k_H) = \rho\sigma + C$). The best line has a slope (ρ) of −2.57, but its correlation coefficient is poor ($r = 0.910$). A much better straight line passes through the points for the meta substituents ($\rho = -3.71$, $r = 0.990$), and the deviations observed for the groups in the para position on the ring are in the direction expected if the Pt–C(aryl) bond was an almost pure σ bond without the ability to transfer ring π effects to the metal.

The kinetic data were also analyzed with the dual-parameter Swain–Lupton equation[27] which enables separation of polar and mesomeric effects and quantitative assessment of their relative importance within the reaction considered. According to this equation a single value of the field constant (*F*) and the resonance constant (*R*) can be associated with each substituent, whether it is in the meta or para position on the ring (see Table VII). The polar parameter (*F*) measures the capability of the substituent to withdraw or release electron density through space and/or the σ-bonding framework, whereas (*R*) measures the ability of the substituent to operate by a resonance interaction.

The calculated effects are

$$\log (k/k_H)_m = f_m F + r_m R + i_m = (-2.18 \pm 0.1)F + (-1.38 \pm 0.14)R + (-0.024 \pm 0.05)$$

$$\log (k/k_H)_p = f_p F + r_p R + i_p = (-1.90 \pm 0.17)F + (-1.58 \pm 0.24)R + (-0.04 \pm 0.09)$$

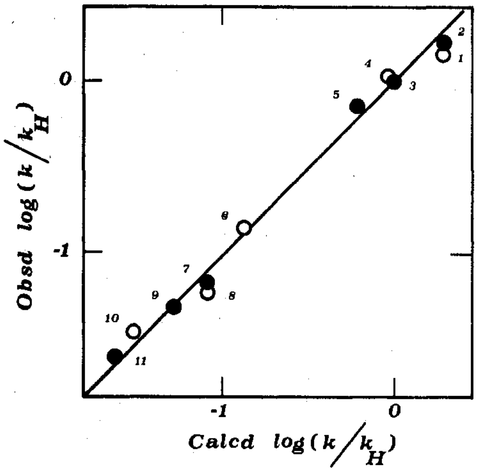


Figure 3. Dual substituent constant plot of para- and meta-substituent effects on the rate of cis–trans isomerization of $[Pt(PEt_3)_2(YC_6H_4)Cl]$ complexes in methanol at 30 °C: 1, *p*-Me; 2, *m*-Me; 3, H; 4, *p*-OMe; 5, *m*-OMe; 6, *p*-F; 7, *m*-F; 8, *p*-Cl; 9, *m*-Cl; 10, *p*-CF_3; 11, *m*-CF_3.

These *f*, *r*, and *i* values together with their standard deviation (±) and correlation coefficients were fitted by a computerized linear least-squares multiple-correlation analysis.

The f_m and f_p reaction constants represent the sensitivities of the isomerization to field effects transmitted by meta and para substituents on the aryl ring. They are comparable (−2.18 and −1.90) and of the expected sign and magnitude, because electron-donating (negative *F*) substituents facilitate departure of Cl^- with its previously bonding electron pair by stabilizing a transition state of structure similar to that of the electron-deficient platinum cation. The r_m and r_p values, which represent the sensitivities of these reactions to the influences transmitted by resonance or π bonds, are also comparable (−1.38 and −1.59) and are of the same sign as f_m and f_p.

The correlation coefficients are 0.995 for the meta and 0.984 for the para substituents. The very good fit illustrated in Figure 3 confirms that the use of the Swain–Lupton equation is appropriate and that only field and resonance influences can account for substituent effects.

The % *R* value, which measures the relative contribution of the resonance to the total effect, is 28% for the meta and 32% for the para substituents. It would seem that, in the isomerization reactions, σ inductive effects are dominant. The participation of the aryl π-bonding system in the stabilization of the transition state is modest and remains fairly constant (28 vs. 32%), irrespective of the position of the substituent on the ring. This constancy argues strongly for the extent of the aryl–platinum π interaction being small and being of secondary importance with respect to σ bonding. As matter of fact, if the amount of π bonding were large, we would have expected a substantial enhancement of resonance effects for the set of para substituents and a larger contribution to the total substituent effect (compare % *R* = 22 and 53% for Hammett's parameters σ_m and σ_p, respectively[27]).

The nature of the Pt^{II}–C(aryl) bond has been probed by ^{13}C and ^{19}F NMR studies,[7,28-30] but no clear-cut conclusion has been reached about the extent of d_π–p_π interactions. Extensive electron withdrawing through π back-donation from platinum to carbon should produce a shortening of the Pt–C bond. Preliminary results of an X-ray diffraction study carried on the complex *trans*-$[Pt(PEt_3)_2(C_6H_5)Cl]$[31] has shown that the Pt–C(aryl) bond distance of 2.03 (2) Å is comparable to the Pt–C(alkyl) bond distance of 2.08 (1) Å found in *trans*-$[Pt(PMe_2Ph)_2(CH_2SiMe_3)Cl]$,[32] once the different covalent radii of sp^2 and sp^3 carbons are taken into account.

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Note Added in Proof. Since the submission of this paper R. van Eldik, D. A. Palmer, and H. Kelm, *Inorg. Chem.*, **18**, 572 (1979), have reported the measure of the volume of activation ($\Delta V^{\ddagger} = -14.1$ cm^3 mol^{-1}) for the methanol solvolysis of *cis*-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br], which we have already shown (cf. ref 3c) to proceed at the same rate and with the same $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as those of its uncatalyzed cis–trans isomerization. The negative value found for $\Delta V^{\ddagger}$ leads these authors to favor an associative mechanism for the isomerization of this complex. They extend this conclusion to all the series of complexes *cis*-[Pt(PEt$_3$)$_2$(R)Br], which according to their view isomerize with a preequilibrium mechanism. By using our data for the isomerization as a function of [Br$^-$] (taken from Table II in ref 3c) and eq 5 Kelm and co-workers estimate the following values for the equilibrium constants K_e (10^4K_e, M (30 °C)): 0.69, R = Ph; 0.75, R = *p*-MeC$_6$H$_4$; 0.73, R = *o*-MeC$_6$H$_4$; 0.49, R = *o*-EtC$_6$H$_4$; 2.1, R = 2,3,6-Me$_3$C$_6$H$_2$. If the values of K_e were in this range, at the low concentrations of complex used for the kinetic runs ($<10^{-4}$ M), the equilibrium in Scheme I should be largely shifted (>60%) toward the solvento species.

Due to the slowness of the isomerization rate, we have been able to perform an independent control of these equilibrium constants by measuring the initial conductance of a 10^{-4} M methanol solution of *cis*-[Pt(PEt$_3$)$_2$(R)Br]. The values of K_e which we have obtained by this method, assuming a value of $\lambda_\infty = 100\ \Omega^{-1}$ cm^{-1} L mol^{-1} for the molar conductivity of a 1:1 electrolyte in methanol, are as follows (10^6K_e, M (30 °C)): 1.84 ± 0.2, R = Ph; 1.97 ± 0.14, R = *p*-MeC$_6$H$_4$; 2.96 ± 0.05, R = *o*-MeC$_6$H$_4$; 0.85 ± 0.08, R = *o*-EtC$_6$H$_4$; 0.27 ± 0.08, R = 2,3,6-Me$_3$C$_6$H$_2$.

These values of K_e account only for a few percent of initial dissociation of the complexes and are a further evidence against the preequilibrium mechanism for the isomerization of *cis*-[Pt(PEt$_3$)$_2$(R)X] complexes.

Registry No. *cis*-[Pt(PEt$_3$)$_2$(Ph)Cl], 15702-92-8; *cis*-[Pt(PEt$_3$)$_2$(*m*-MeC$_6$H$_4$)Cl], 70445-93-1; *cis*-[Pt(PEt$_3$)$_2$(*p*-MeC$_6$H$_4$)Cl], 67112-04-3; *cis*-[Pt(PEt$_3$)$_2$(*m*-OMeC$_6$H$_4$)Cl], 67049-23-4; *cis*-[Pt(PEt$_3$)$_2$(*p*-OMeC$_6$H$_4$)Cl], 67112-04-3; *cis*-[Pt(PEt$_3$)$_2$(*m*-FC$_6$H$_4$)Cl], 15169-92-3; *cis*-[Pt(PEt$_3$)$_2$(*p*-FC$_6$H$_4$)Cl], 15169-93-4; *cis*-[Pt(PEt$_3$)$_2$(*m*-ClC$_6$H$_4$)Cl], 67049-39-2; *cis*-[Pt(PEt$_3$)$_2$(*p*-ClC$_6$H$_4$)Cl], 67112-05-4; *cis*-[Pt(PEt$_3$)$_2$(*m*-CF$_3$C$_6$H$_4$)Cl], 67049-39-2; *cis*-[Pt(PEt$_3$)$_2$(*p*-CF$_3$C$_6$H$_4$)Cl], 67049-38-1; *cis*-[Pt(PEt$_3$)$_2$(Ph)I], 56553-44-7; *cis*-[Pt(PEt$_3$)$_2$(C$_6$F$_5$)Cl], 14494-02-1; *cis*-[Pt(PEt$_3$)$_2$Cl$_2$], 15692-07-6.

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