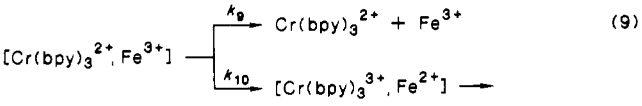
importance of the term $k_{Cr}[Cr(bpy)_3^{2+}]$ during the reaction is apparently gradual enough that it does not affect the quality of the pseudo-first-order fits significantly. Indeed, the simulation of the kinetic traces by use of the program KINSIM shows this to be the case.

The low yields of $Cr(bpy)_3^{2+}$ obtained previously[14] in the reduction of $^*Cr(bpy)_3^{3+}$ by Fe^{2+} in 1 M $HClO_4$ were rationalized on the basis of eq 8–10. According to this scheme the $Cr(bpy)_3^{2+}$

$$^*Cr(bpy)_3^{3+} + Fe^{2+} \rightarrow [Cr(bpy)_3^{2+},Fe^{3+}] \qquad (8)$$

and Fe^{3+}, formed by electron transfer, can either escape from the solvent cage (eq 9) or undergo secondary electron transfer within the cage to yield Fe^{2+} and $Cr(bpy)_3^{3+}$ (eq 10). On the basis of the yields of $Cr(bpy)_3^{2+}$ the ratio $k_9/k_{10} \sim 0.2$ was calculated.[14]



$$[Cr(bpy)_3^{2+},Fe^{3+}] \xrightarrow{k_9} Cr(bpy)_3^{2+} + Fe^{3+} \qquad (9)$$

$$[Cr(bpy)_3^{2+},Fe^{3+}] \xrightarrow{k_{10}} [Cr(bpy)_3^{3+},Fe^{2+}] \rightarrow Cr(bpy)_3^{3+} + Fe^{2+} \qquad (10)$$

Our results indicate that the yield of $Cr(bpy)_3^{2+}$ is nearly quantitative (≥80%) provided the concentration of Fe^{2+} used is high enough such that the second term of eq 6 dominates. For example, in an experiment with $[^*Cr(bpy)_3^{3+}]_0 = 40\ \mu M$ and $[Fe^{2+}] = 0.18$ M, the concentration of $Cr(bpy)_3^{2+}$ produced was 35 μM. We thus conclude that most of the electron transfer events of eq 8 lead to the formation of free $Cr(bpy)_3^{2+}$ and Fe^{3+}, with the secondary electron transfer within the solvent cage playing at best a minor role, i.e. $k_9 \gg k_{10}$. This experimental result agrees well with the values of k_9 ($\sim 10^{10}\ s^{-1}$) and k_{10} ($\sim 10^9\ s^{-1}$) estimated from the theoretical equations[26] and the measured value of k_2 ($k_2 = k_{10}K_{IP}$, $K_{IP} \sim 1$).[26,27] The predicted yield of $Cr(bpy)_3^{2+}$ ($k_9/(k_9 + k_{10}) \sim 0.9$) is in good agreement with the observed value (≥0.80). We surmise that the low experimental concentrations of Fe^{2+}, as well as the use of the somewhat erroneous spectral data for $^*Cr(bpy)_3^{3+}$, are responsible for the low values of k_9/k_{10} reported in ref 14.

The large driving force (1.71 eV) for the net reaction of eq 4, combined with the high self-exchange rate constants for the two reactants, places reaction 4 in the inverted region, yet the reaction is clearly diffusion-controlled. The same observation was made in several other highly exergonic reductions by $Cr(bpy)_3^{2+}$.[9,28] Among the many factors[11,28-31] that could be responsible for the rate constants being higher than predicted, the formation of excited-state $Cr(bpy)_3^{2+}$ (eq 11) and nuclear tunneling[9,11,28] seem

$$^*Cr(bpy)_3^{3+} + Cr(bpy)_3^{2+} \rightarrow {}^*Cr(bpy)_3^{2+} + Cr(bpy)_3^{3+} \qquad (11)$$

most plausible. The products of reaction 11 are identical with those that would be formed in an energy-transfer process. At present we do not have sufficient experimental evidence that would allow us to distinguish between the possibilities mentioned.

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Registry No. $Cr(bpy)_3^{3+}$, 15276-15-0; Fe^{2+}, 15438-31-0; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Cr(bpy)_3^{2+}$, 15276-15-0; $[Cr(bpy)_3](ClO_4)_3$, 23539-86-8; ClO_4^-, 14797-73-0; Cl^-, 16887-00-6; SO_4^{2-}, 14808-79-8.

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Selective Cleavage of the Pt–C(Alkyl) Bond in Alkylarylplatinum(II) Complexes and Mechanism of Cis to Trans Isomerization of the Resulting Solvento Complexes

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Protonolysis of the complexes *cis*-$[Pt(PEt_3)_2(R)(Me)]$ (R = Me, Ph, mesityl) by H^+A^- ($A^- = ClO_4^-$, BF_4^-, *p*-toluenesulfonate) in methanol selectively cleaves the alkyl group, yielding *cis*-$[Pt(PEt_3)_2(R)(MeOH)]^+$ and methane. The rates show first-order dependence on complex and on proton concentrations, obeying the simple rate law $k_{obsd} = k_H[H^+]$. Steric hindrance on the Pt–C bond causes a decrease in rate. A mechanism is proposed that involves rate-determining attack of the proton on the Pt–C bond with release of methane in a three-center transition state. The resulting methanol intermediate spontaneously converts to its trans isomer, and for all systems the isomeric equilibrium lies well to the side of the trans form. At 303.16 K for R = Me, $k_i = 6.76 \times 10^{-3}\ s^{-1}$, $\Delta H^{\ddagger} = 106 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger} = +63 \pm 12$ J K^{-1} mol^{-1}; for R = Ph, $k_i = 11.9 \times 10^{-3}\ s^{-1}$, $\Delta H^{\ddagger} = 112 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = +84 \pm 8$ J K^{-1} mol^{-1}; for R = mesityl, $k_i = 28.8 \times 10^{-3}\ s^{-1}$, $\Delta H^{\ddagger} = 106 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = +75 \pm 8$ J K^{-1} mol^{-1}. Isomerization of *cis*-$[Pt(PEt_3)_2(Me)(MeOH)]^+$ in diethyl ether–methanol mixtures undergoes mass law retardation by [MeOH]. The rates of isomerization of *cis*-$[Pt(PEt_3)_2(Me)(S)]^+$ (S = a series of hydroxylic solvents) are little influenced by the nature of the solvent. As in the case of the related halide species, the isomerization mechanism involves interconversion of two T-shaped 3-coordinate intermediates that show discriminating ability toward scavenging agents.

Introduction

Studies on the isomerization reactions of square-planar organometallic compounds are of fundamental importance for understanding the chemical reactivity of these species. Indeed, the course of many processes is dictated by the geometry in the square-planar configuration. For example, one reaction scheme postulated for olefin insertion on trans platinum(II) hydrides involves the isomerization of a 4-coordinated *trans*-$[Pt(PEt_3)_2(H)(C_2H_4)]^+$ cation to its cis counterpart followed by migratory insertion leading to the final monoalkyl complex.[1] Dialkylbis(phosphine)palladium(II) complexes give strikingly different products in their thermolysis or reactions with CO depending on configuration.[2] For concerted thermal 1,1-reductive elimination

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to take place, it has been argued that the organic moieties should be brought to occupy adjacent positions in the complex prior to giving a C–C coupling product[3] as for the case of *trans*-[PdMe$_2$L$_2$] (L = phosphine) where trans–cis isomerization first takes place followed by reductive elimination of ethane.[4]

There are a number of conceivable pathways by which isomerization can proceed.[5] One of them involves the conversion of two T-shaped 3-coordinate intermediates, as originally postulated for uncatalyzed isomerization of monoaryl *cis*-[Pt(PEt$_3$)$_2$(R)Cl] complexes.[6] It is now clear that the formation of such 3-coordinate 14-electron species, whose configurational stability has been supported by MO calculations,[7] offers a favorable reaction route to all the above mentioned processes as an alternative to the intermediacy of 4- and 5-coordinate species.[5,8] In this context it is of fundamental importance to understanding the factors promoting the formation and the stabilization of these unsaturated species, as well as the efficiency with which they can be intercepted in solution by ligands or by the solvent itself. To this purpose, studies on isomerization of solvento complexes can be useful and have not been reported before.

We report here a kinetic study of the protonolysis of the Pt–Me bond in *cis*-[Pt(PEt$_3$)$_2$(R)(Me)] (R = Me, Ph, mes (mes = mesityl)) complexes in methanol and of the cis to trans isomerization of *cis*-[Pt(PEt$_3$)$_2$(R)(MeOH)]$^+$ formed in situ. The rates of isomerization of *cis*-[Pt(PEt$_3$)$_2$(Me)(S)]$^+$ (S = a series of hydroxylic solvents) have been also measured and compared with those for isomerization of the related chloride complex. These data will be discussed within the framework of the known mechanistic patterns for these reactions and will serve, we hope, to settle a long standing dispute on the mechanism of isomerization of monoorganoplatinum(II) complexes.

Experimental Section

Preparation of Complexes. *cis*-[Pt(PEt$_3$)$_2$(Me)$_2$], *cis*-[Pt(PEt$_3$)$_2$(Ph)Cl], *cis*-[Pt(PEt$_3$)$_2$(mes)Br], and *cis*- and *trans*-[Pt(PEt$_3$)$_2$(Me)Cl] were prepared by literature methods[9] and characterized by elemental analysis, ^{1}H and ^{31}P{^{1}H} NMR spectra.

***cis*-[Pt(PEt$_3$)$_2$(Ph)(Me)].** Methyllithium in diethyl ether (6.0 cm^3, 0.5 M solution) was added dropwise to a suspension of *cis*-[Pt(PEt$_3$)$_2$(Ph)Cl] (0.16 g) in diethyl ether (40 cm^3) under an atmosphere of N$_2$. After 1 h of stirring at room temperature, the mixture was hydrolyzed with ice and water. The crude product isolated from the dried organic layer was crystallized (at −20 °C) as a white compound from petroleum ether, mp 80.0 °C. Anal. Calcd for C$_{19}$H$_{38}$P$_2$Pt: C, 43.6; H, 7.3. Found: C, 43.6; H, 7.2. ^{1}H NMR (CD$_2$Cl$_2$): δ(MePt) 0.21 (dd, ^3J(PH) = 7.9, 6.3 Hz, ^2J(PtH) = 68 Hz). ^{31}P{^{1}H} NMR in (CD$_3$)$_2$CO (AB and ABX; X = ^{195}Pt): δ(^{31}P) 6.23 (^2J(PP) = 13 Hz, ^1J(PtP) = 1837 Hz); 6.45 (^1J(PtP) = 1727 Hz).

***cis*-[Pt(PEt$_3$)$_2$(mes)(Me)].** This was prepared in an analogous manner from *cis*-[Pt(PEt$_3$)$_2$(mes)Br] (0.3 g) and methyllithium (3-fold excess). The mixture was stirred at room temperature for 4 h and then hydrolized with ice. The dried organic layer was evaporated under vacuum to give the product as a white solid, mp 169–170 °C. Anal. Calcd for C$_{22}$H$_{44}$P$_2$Pt: C, 46.7; H, 7.8. Found: C, 46.7; H, 7.7. ^{1}H NMR (CD$_2$Cl$_2$): δ(MePt) 0.1 (dd, ^3J(PH) = 8.7, 6.6 Hz, ^2J(PtH) = 67 Hz), δ(4-MeC) 2.15 (s), δ(2,6-MeC) 2.30 (t). ^{31}P{^{1}H} NMR in (CD$_3$)$_2$CO: δ(^{31}P) 2.79 (^2J(PP) = 12.36 Hz, ^1J(PtP) = 1914 Hz), 6.26 (^1J(PtP) = 1748 Hz).

^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with a Perkin-Elmer R 24B or a Varian FT 80A spectrometer. Phosphorus-31 chemical shifts are given with respect to an H$_3$PO$_4$ reference. Ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol were purified and dried by standard methods. All the other chemical products were reagent grade commercial materials and were used without further purification.

Methanol for conductometric measurements was refluxed over AgNO$_3$ for 24 h to remove traces of aldehydes or ketones and then distilled in a closed system into a flask containing some magnesium turnings and traces of I$_2$. After a further 24 h of refluxing, it was fractionally distilled. The middle cut was used immediately after distillation. Conductance data were measured by using a Radiometer CDM3 conductivity bridge and an Erlenmeyer-type cell with unplatinized electrodes and with a constant of 0.5693 cm^{-1} determined by using solutions of potassium chloride. Conductance measurements were taken soon after weighed amounts of complex in silver holders had been rapidly dissolved under magnetic stirring in weighed amounts of methanol in the conductance cell. The temperature was held constant to ±0.01 °C with a thermostated bath. Limiting equivalent conductances Λ_0 and association constants K_a were calculated by computer analysis using the equations

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2}$$

$$1 - \gamma = K_a c\gamma^2 f^2$$

where c is the stoichiometric concentration, $c\gamma$ is the concentration of free ions, S is the slope of the theoretical limiting tangent, and f is the Debye–Hückel value of the activity coefficients.[10] A viscosity of 0.502 cP and dielectric constant of 31.7 were used in the calculations.

Kinetics. Isomerization reactions were followed spectrophotometrically by repetitive scanning of the spectrum at suitable times in the range 320–220 nm or at a fixed wavelength, where the difference of absorbance was largest. The reactions were carried out in a silica cell in the thermostated cell compartment of a Cary 219 spectrophotometer with a temperature accuracy of ±0.02 °C. The isomerization of *cis*-[Pt(PEt$_3$)$_2$(Me)Cl] was started by adding a weighed amount of a finely powdered sample of the complex to a prethermostated volume of solvent and shaking the solution rapidly. The isomerization of *cis*-[Pt(PEt$_3$)$_2$(R)(MeOH)]$^+$ (R = Me, Ph, mes) generated in situ was started by adding with a syringe a prethermostated solution of *cis*-[Pt(PEt$_3$)$_2$(R)(Me)] to a methanolic thermostated solution of H$^+$A$^-$ (A$^-$ = BF$_4^-$, ClO$_4^-$, *p*-toluenesulfonate). In all the cases the concentration of acid was calculated to produce a very fast cleavage of the Pt–Me bond. In an analogous way were followed the rates of isomerization of *cis*[Pt(PEt$_3$)$_2$(Me)(S)]$^+$ (S = ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-2-propanol) and those of *cis*[Pt(PEt$_3$)$_2$(Me)(MeOH)]$^+$ in methanol–diethyl ether mixtures. Reactions of nucleophilic substitutions of *cis*[Pt(PEt$_3$)$_2$(Me)Cl] with LiI and electrophilic attacks of H$^+$ on *cis*-[Pt(PEt$_3$)$_2$(R)(Me)], except the case in which R = mes, required the use of a HI-TECH SF3 stopped-flow spectrophotometer equipped with a Gould 054100 oscilloscope and a Radiometer REC 61 potentiometric recorder. The kinetics were performed under pseudo-first-order conditions, and the rate constants k_{obsd} were obtained from a nonlinear least-squares fit of the experimental data to $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{\mathrm{obsd}}t)$ with A_0, A_∞, and k_{obsd} as the parameters to be optimized (A_0 = absorbance after mixing of reagents; A_∞ = absorbance at completion of reaction). Activation parameters were derived from a nonlinear fit of k/T vs T data according to the Eyring formalism.

Results

The methylarylplatinum complexes *cis*-[Pt(PEt$_3$)$_2$(R)(Me)] (R = Ph and mes) were prepared from the corresponding aryl halide complexes (eq 1). The desired products were obtained in high

$$cis\text{-}[\mathrm{Pt(PEt_3)_2(R)X}] + \mathrm{LiMe} \rightarrow cis\text{-}[\mathrm{Pt(PEt_3)_2(R)(Me)}] + \mathrm{LiX} \quad (1)$$

purity and without the difficulties reported by Puddephatt[11] for the synthesis of related compounds with dimethylphenylphosphine. The mesityl complex gave normal first-order ^{1}H and ^{31}P NMR spectra with a methylplatinum resonance appearing as four lines of equal intensity due to coupling to two nonequivalent ^{31}P atoms, two ^{31}P resonances each showing a low ^{1}J(PtP) coupling constant, and a low value of ^{2}J(PP) of 12 Hz typical for cis phosphines. The two inequivalent PEt$_3$ ligands in the phenyl complex gave a strongly coupled AB pattern with a consequent ABX$_3$ pattern

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Table I. Rate Constants for the Selective Cleavage of the Pt–CH_3 Bond upon Proton Attack on the Complexes *cis*-$[Pt(PEt_3)_2(R)(Me)]$[a]

$10^3[H^+]$, M	$[Cl^-]$, M	k_{obsd}, s^{-1}	$10^3[H^+]$, M	$[Cl^-]$, M	k_{obsd}, s^{-1}
		R = Me[b]			
0.25	0.00	18.8	1.00	0.05	72.4
0.50	0.00	37.6	1.00	0.10	74.1
1.00	0.00	74.9	1.00	0.20	75.1
1.00	0.01	76.7			
		R = Ph[c]			
0.25	0.00	0.80	1.00	0.05	3.19
0.50	0.00	1.62	1.00	0.10	3.19
1.00	0.00	3.24	1.00	0.20	3.28
1.00	0.01	3.12	2.00	0.00	6.53
		R = mes[d]			
0.80	0.02	0.0108	1.00	0.10	0.0136
1.00	0.01	0.0138	1.00	0.20	0.0138
1.00	0.02	0.0142	2.00	0.02	0.0272
1.00	0.05	0.0136	3.00	0.02	0.0410

[a] In MeOH at 303.2 K. [b] $k_H = (743 \pm 20) \times 10^2\ M^{-1}\ s^{-1}$. [c] $k_H = (32.7 \pm 0.4) \times 10^2\ M^{-1}\ s^{-1}$. [d] $k_H = (0.14 \pm 0.002) \times 10^2\ M^{-1}\ s^{-1}$.

for the Pt–Me ^1H NMR signal.

Selective Cleavage of the Pt–Me Bond. The cleavage of the Pt–CH_3 σ bond by protonolysis takes place according to the reactions

$$cis\text{-}[Pt(PEt_3)_2(R)(Me)] \xrightarrow[MeOH]{H^+Cl^-} cis\text{-}[Pt(PEt_3)_2(R)Cl] + CH_4 \qquad (2)$$

R = Me, Ph, mes

When reactions are carried out in the presence of excess of chloride ion the final monoaryl complexes retain the same cis configuration as their parent methylaryl substrates. In the absence of chloride ion, the cleavage of the Pt–Me bond is followed by isomerization of *cis*-$[Pt(PEt_3)_2(R)(S)]^+$ (S = MeOH) to the trans monoaryl analogues. The products from protonolysis reactions were identified by comparison of the final spectra with those of corresponding authentic samples of *cis*- and *trans*-$[Pt(PEt_3)_2(R)Cl]$ that had been prepared independently. The protonolysis of the mesityl complex was followed by the usual spectrophotometric methods. The other reactions, all faster, were followed by means of a stopped-flow apparatus. The pseudo-first-order rate constants k_{obsd} (s^{-1}) for (2) are listed in Table I for a range of H^+ and Cl^- concentrations at 30 °C. The k_{obsd} values were linearly dependent on proton concentration; i.e., $k_{obsd} = k_H[H^+]$. The values of k_H, from linear regression analysis of the rate law, are set forth in Table I (uncertainties are standard errors of estimates).

Isomerization of *cis*-$[Pt(PEt_3)_2(R)(MeOH)]^+$. The solvento complexes formed upon selective cleavage of the Pt–CH_3 bond in methanol undergo spontaneous isomerization to their trans form. The process can be followed very clearly by $^{31}P\{^1H\}$ NMR. For example, *cis*-$[Pt(PEt_3)_2(Me)_2]$ in CD_3OD at −60 °C gives a ^{31}P resonance at δ 8.81 ($^1J(PtP)$ = 1839 Hz). Upon addition of a sufficient excess of ethereal solution of HBF_4 there is an immediate and sharp change of the spectrum, which now shows two ^{31}P resonances, $\delta(P_A) = 7.91$ ($^1J(PtP_A)$ = 1829 Hz) and $\delta(P_B) = 23.87$ ($^1J(PtP_B)$ = 4344 Hz, $^2J(PP)$ = 13.0 Hz). The low coupling constant $^1J(PtP_A)$ is typical of phosphorus atoms trans to carbon in platinum complexes, while the value $^1J(PtP_B)$ = 4344 Hz is consistent with the presence of a very weak trans donor ligand such as MeOH. Thus, the cis configuration is retained as a result of the Pt–CH_3 bond breaking, as evidenced also by the low value of the $^2J(PP)$ coupling constant. Essentially the same pattern is observed when the proton attack is carried out with $HClO_4$ or *p*-toluenesulfonic acid, except that there is some evidence for the contemporary presence in solution of small amounts of species containing a direct bond between the metal and the counterions. At 283.16 K isomerization can be monitored by ^{31}P NMR through the decrease in the signals associated with *cis*-$[Pt(PEt_3)_2(Me)(MeOH)]^+$ and the parallel and matching increase in the signal of corresponding trans complex, which appears at δ 25.14 with a $^1J(PtP)$ = 2786 Hz.

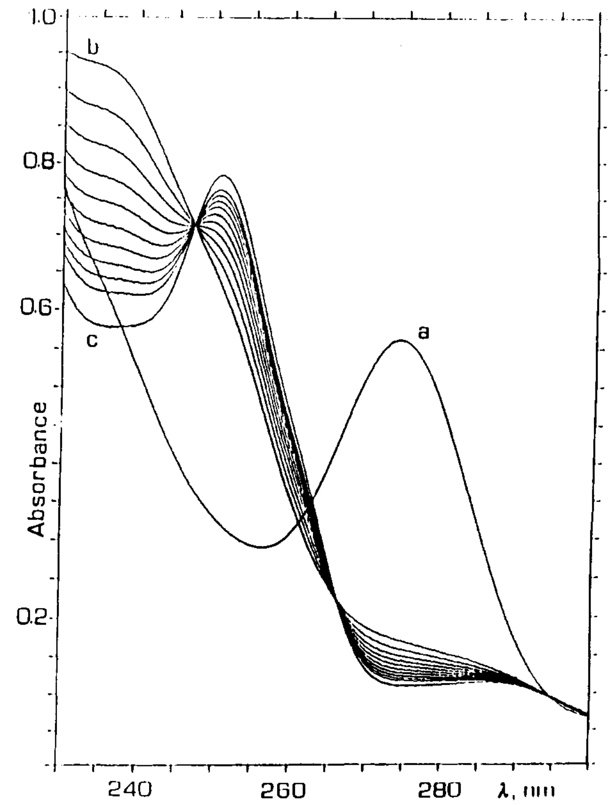


Figure 1. Electronic spectrum of *cis*-$[Pt(PEt_3)_2(Me)_2]$ in methanol at 20 °C (a) and spectral changes (b–c) associated with cis to trans isomerization of $[Pt(PEt_3)_2(Me)(MeOH)]^+$ generated in situ.

Table II. Temperature Effect on the Rates of Isomerization of Solvento *cis*-$[Pt(PEt_3)_2(R)(MeOH)]^+$ Complexes

t, K	10^3k_{obsd}, s^{-1}	*t*, K	10^3k_{obsd}, s^{-1}
	R = Me[a]		
288.16	0.583	303.16	6.76
293.16	1.44	308.16	12.7
297.16	2.66	313.16	21.5
	R = Ph[b]		
288.16	1.00	303.16	11.9
293.5	2.57	308.16	21.7
298.16	4.74	313.16	45.7
	R = mes[c]		
289.1	3.60	298.5	15.3
293.16	6.48	303.16	28.8

[a] $\Delta H^\ddagger$ = 106 ± 4 kJ mol^{-1}; $\Delta S^\ddagger$ = +63 ± 12 J K^{-1} mol^{-1}. [b] $\Delta H^\ddagger$ = 112 ± 3 kJ mol^{-1}; $\Delta S^\ddagger$ = +84 ± 8 J K^{-1} mol^{-1}. [c] $\Delta H^\ddagger$ = 106 ± 3 kJ mol^{-1}; $\Delta S^\ddagger$ = +75 ± 8 J K^{-1} mol^{-1}.

Table III. Mass Law Retardation Produced by Chloride on the Rates of Isomerization of *cis*-$[Pt(PEt_3)_2(Me)Cl]$ in Methanol[a] and by Methanol on the Rates of Isomerization of *cis*-$[Pt(PEt_3)_2(Me)(MeOH)]^+$ in Diethyl Ether–Methanol Mixtures[b]

cis-$[Pt(PEt_3)_2(Me)Cl]$		*cis*-$[Pt(PEt_3)_2(Me)(MeOH)]^+$	
$10^3[Cl^-]$, M	10^3k_{obsd}, s^{-1}	[MeOH], M	10^3k_{obsd}, s^{-1}
0.0	1.54	0.246	18.1
0.1	0.691	0.493	13.8
0.2	0.463	0.871	10.1
0.4	0.270	1.23	7.85
1.0	0.120	1.97	5.22
1.2	0.105	2.47	4.31
		3.70	2.97
		3.95	2.88
		4.93	2.40

[a] At 303.16 K. [b] At 293.16 K.

Table IV. Effect of Changing the Nature of the Solvent on the Rates of Isomerization of *cis*-[Pt(PEt$_3$)$_2$(Me)X] Complexes at 303.16 K

solvent	10^3k_i, s^{-1} X = Cl$^-$	 X = solvent
methanol	1.27	6.76
ethanol	0.090	3.83
1-propanol	0.040	2.40
1-butanol		2.44
2-propanol	0.0088	2.52
2-methyl-2-propanol		0.70

However, visible/UV spectrophotometric techniques offer the advantage over ^{31}P NMR, among others, of requiring far less complex for the kinetic study, so the reactions were followed by repetitive scanning of the spectrum in the UV region (Figure 1). The pseudo-first-order rate constants k_i (s^{-1}) for isomerization of *cis*-[Pt(PEt$_3$) = (R)(MeOH)]$^+$ (R = Me, Ph, mes) at various temperatures together with the associated activation parameters are set forth in Table II. The rate constants k_i (s^{-1}) for isomerization of *cis*-[Pt(PEt$_3$)$_2$(Me)(MeOH)]$^+$ in methanol–diethyl ether mixtures are listed in Table III, and those for isomerization of *cis*-[Pt(PEt$_3$)$_2$(Me)(S)]$^+$ (S = a series of hydroxylic solvents at 30 °C) are listed in Table IV.

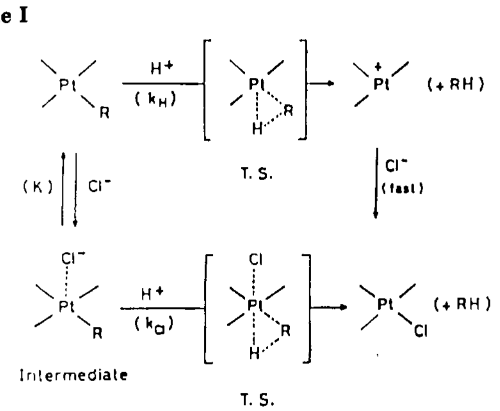
Discussion

Electrophilic Attacks. When this work began, the aim in preparing *cis*-[Pt(PEt$_3$)$_2$(R)(Me)] complexes was to have suitable precursors for the formation of solvento species in methanol, and in order to avoid any interference with the subsequent isomerization, it was necessary to measure the effect of acids on the rates of Pt–CH$_3$ bond breaking. Now that the proper kinetic study has been done, the whole set of data can be discussed within the framework of the mechanistic patterns for electrophilic cleavage of the metal–carbon bond in platinum(II) complexes. This is especially intriguing for the problem of the selectivity of the site attack which, in principle, can take place by (i) direct attack on the Pt–C bond, (ii) attack on the aromatic ring in the case of aryl derivatives, and (iii) a prior oxidative addition on the metal followed by reductive elimination (S$_E$(oxidative) mechanism). The kinetics of acidolysis of several halo alkyl-,[12] diaryl-,[13] and alkylarylplatinum complexes have been studied in some detail, and the factors taken into consideration, among others, to support a given reaction pathway include (i) the form of the rate law, (ii) the halide ion dependence, (iii) the nature of the other ligands on the metal, and (iv) the relative energies of the Pt–C σ-bonding MO and of the nonbonding 5d orbitals.

As far as alkyl vs aryl cleavage in platinum complexes is concerned, the only two systematic studies in the field have led to conflicting interpretations. The preferential cleavage of the alkyl rather than the aryl group in the complexes *cis*-[Pt(L)$_2$(R)(Me)] (L = PMe$_2$Ph, R = Ph, *p*-MeC$_6$H$_4$) has been taken by Puddephatt et al.[11] as evidence for an oxidative-addition–reductive-elimination mechanism. This conclusion has been disputed mainly on the basis of the large kinetic isotope effect observed for protonolysis of the Pt–Me bond in *trans*-[Pt(PEt$_3$)$_2$(Ar)(Me)][14] or of an aryl–platinum bond in *cis*-[Pt(PEt$_3$)$_2$(Ar)$_2$],[13] which strongly suggests a rate-determining transfer of the proton to the Pt–C bond and militates against a multistep S$_E$(oxidative) mechanism.

We still favor this one-step proton transfer mechanism for (2) whose rates show a linear dependence on [H$^+$] and independence of [Cl$^-$], obeying the rate law $k_{\mathrm{obsd}} = k_H[H^+]$. As expected, the bulk at the protonation site brought about by the cis group plays an adverse role, giving the sequence of reactivity methyl > phenyl >> mesityl in the ratio 1:0.13:0.0002. According to the results of some recent studies,[15] the simple rate law observed would be a reduced form of a bivariate nonlinear rate law

Scheme I



$$k_{\mathrm{obsd}} = \frac{k_H + k_{Cl}K[Cl^-]}{1 + K[Cl^-]}[H^+] \qquad (3)$$

which has been observed with complexes where withdrawal of electron density from the metal promotes the formation of a halide intermediate adduct with the substrate. The mechanism proposed (Scheme I) is thought to rationalize all the previously reported kinetic results (in particular the diverse chloride ion dependency) within an unified picture, and involves a fast preequilibrium formation of a platinum(II) anionic intermediate via interaction of the halide with the square-planar substrate (K), combined with slow, parallel protonation of both the substrate (k_H) and the intermediate (k_{Cl}), causing the cleavage of the metal σ bond. In the system under study, K seems to be exceedingly low (no kinetically appreciable formation of the halide intermediate takes place).

Spontaneous Isomerization of Solvento Complexes. As described above the spontaneous conversion of *cis*-[Pt(PEt$_3$)$_2$(R)(S)]$^+$ (R = Me, Ph, mes; S = solvent) can be conveniently followed either by ^{31}P{^{1}H}NMR or conventional spectrophotometric techniques. The spectral changes in the UV region (Figure 1) show well-defined isosbestic points confirming that the two isomers are the only absorbing species in solution. The conversion is complete, the trans isomer is the only species at the end of the reaction, and the process follows a first-order rate law. In the case of the methanol complexes (Table II) the rate of isomerization is almost insensitive to steric crowding produced by the cis group, increasing by a factor of 4 on going from methyl to mesityl. The trend is opposite to that observed for bimolecular processes, as the electrophilic attacks described above or nucleophilic substitutions, where the destabilization of the five-coordinate transition state produced by the *o*-methyl groups in the mesityl ring provokes a decrease in rate of at least 5 orders of magnitude with respect to that of phenyl.[16] This pattern is consistent with a mechanism in which the breaking of the Pt–S bond is the most important factor in determining the rate. The formation of a 3-coordinate T-shaped intermediate, which maintains memory of the original structure, does not require relief of steric strain to the remaining ligands, which essentially keep their original position around the metal. The high values of ΔH^* and the largely positive values of ΔS^* agree with a dissociative mechanism.

Mass law retardation experiments were carried out following the rate of conversion of *cis*-[Pt(PEt$_3$)$_2$(Me)(MeOH)]$^+$ in mixtures of different compositions of methanol–diethyl ether. The choice of the latter solvent has been dictated by the need of having a

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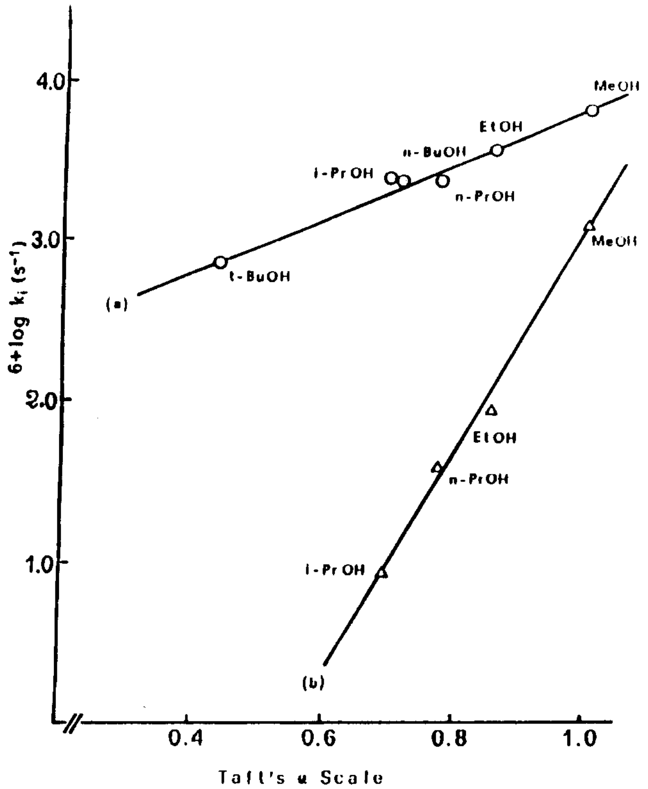


Figure 2. Correlation plot of the rates of uncatalyzed isomerization of *cis*-$[Pt(PEt_3)_2(Me)(S)]^+$ (a) and of *cis*-$[Pt(PEt_3)_2(Me)Cl]$ (b) with the hydrogen-bonding donor (HBD) properties of the solvents.

cosolvent of very poor coordinating ability that is transparent in the UV region. The data in Table III show that indeed there is mass law retardation by MeOH, but this is very much less than that produced by chloride ion in the isomerization of the corresponding chloride complex.

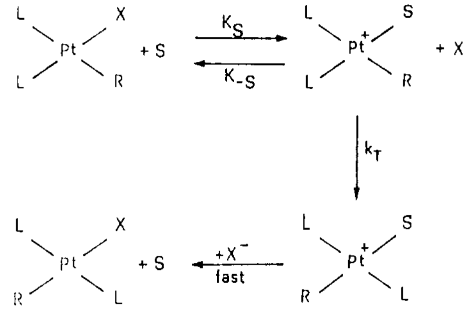
Data in Table IV refer to the effect of changing the nature of solvent on the rates of isomerization of *cis*-$[Pt(PEt_3)_2(Me)X]$ (X = Cl^- or a series of hydroxylic solvents). Analysis of solvent effects on isomerization rate constants of complexes of the type *cis*-$[Pt(PEt_3)_2(R)Cl]$ (R = 4-MeC_6H_4 or 4-FC_6H_4), with special reference to transfer chemical potential for leaving chloride, strongly favored the dissociative mechanism.[17] In protic solvents, electrophilic solvation of Cl^- through hydrogen bonding is the major factor determining the differences in rates observed. The two series of data in Table IV are illustrated in Figure 2, where the logarithms of the rate constants are plotted against Taft's α scale, which is a measure of the electrophilicity of the solvent or more specifically of its hydrogen-bonding ability toward the anion.[18] As expected, the rate of isomerization of the chloride complex is extremely sensitive to changes in the nature of the solvent, showing a decrease in rate of at least 2 orders of magnitude on going from methanol to 2-propanol. By way of contrast, the rate of isomerization of the various solvento complexes $[Pt(PEt_3)_2(Me)(S)]^+$ do not vary markedly along the series examined. This behavior is in keeping with the minor effectiveness of uncoordinated molecules of solvent in assisting the removal of the coordinated one. Similar linear free-energy relationships (LFER) can be obtained by using other popular parameters of solvent electrophilicity[19] such as Grunwald–Winstein's *Y*, Dimroth–Reichardt's E_T, or Kosower's *Z*. The results reveal that the rates of isomerization of chloride and solvento complexes tend to diverge markedly as the ability of the solvent to assist Pt–Cl bond breaking decreases. If one considers the possible modes of solvent interactions influencing the dissociative process, these can be restricted to two factors of overriding importance: solvent "electrophilicity" and solvent "nucleophilicity". The first factor plays a major role in the removal of the leaving group, especially if this implies charge separation, while the latter is important in the subsequent block of the vacant coordination site. This explains why *cis*-$[Pt(PEt_3)_2(R)X]$ (X = alkyl, aryl, halide) complexes maintain their stereochemistry in apolar solvents, but easily isomerize after the break of the Pt–X σ bond.

Table V. Temperature Effect on the Rates of Isomerization and Solvolysis of *cis*-$[Pt(PEt_3)_2(Me)Cl]$ in Methanol

isomerization		solvolysis	
t, K	10^3k_{obsd}, s^{-1}	*t*, K	k_{obsd}, s^{-1}
293.16	0.211	285.7	4.47
298.16	0.496	291.16	5.75
303.16	1.27	303.16	12.6
308.16	2.73	313.16	18.8
313.16	6.05		

$\Delta H^\ddagger = 126 \pm 2$ kJ mol^{-1} $\Delta H^\ddagger = 38 \pm 3$ kJ mol^{-1}
$\Delta S^\ddagger = +112 \pm 8$ J K^{-1} mol^{-1} $\Delta S^\ddagger = -100 \pm 8$ J K^{-1} mol^{-1}

Scheme II



Comparison of Mechanisms. All of the previous kinetic studies on *cis*-$[Pt(PEt_3)_2(R)X]$ complexes have shown that, except for the case of the sterically crowded *cis*-$[Pt(PEt_3)_2(mes)Br]$ complex, the rate constants for solvolysis (k_S) are several orders of magnitude greater than those for isomerization (k_i). In addition, the two processes show completely different characteristics, giving opposite responses to structural changes produced in the substrates or in the reaction medium. This is still true for *cis*-$[Pt(PEt_3)_2(Me)Cl]$, as shown by the comparison of the data in Table V. Observations of this type have led to remove from consideration a "solvolytic" mechanism (Scheme II) that involves reversible release of the halide ion during an associative attack by the solvent followed by isomerization of the solvento intermediate. The rate law that can be derived from this reaction scheme

$$k_i = \frac{k_S}{1 + (k_{-S}/k_T)[X^-]} \tag{4}$$

has the same form of that found experimentally. Equation 4 simplifies to $k_i = k_S$, in the absence of added halide ion, and therefore requires that the rate constant for unretarted isomerization have the same value as the rate constant for unretarted solvolysis. The actual measure of the rate constant for isomerization of *cis*-$[Pt(PEt_3)_2(Me)(MeOH)]^+$ gives further support to this conclusion. As matter of fact, this species is formed from *cis*-$[Pt(PEt_3)_2(Me)Cl]$ at a rate of 12.6 s^{-1} at 30 °C in methanol (Table V) while its isomerization takes a much longer time with a rate constant of 6.76×10^{-3} s^{-1} (Table II).

Because solvolysis of the halide species is fast and reversible (anation of *cis*-$[Pt(PEt_3)_2(R)(MeOH)]^+$ is too fast to measure) and isomerization of the solvento species relatively slow (k_S and $k_{-S} \gg k_T$) it is possible to apply a preequilibrium treatment to Scheme II that leads to the rate law given in (5), where K_e =

$$k_i = \frac{k_T}{1 + K_e^{-1}[X^-]} \tag{5}$$

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Table VI. Values of the Equilibrium Constants for the Reaction *cis*-$[Pt(PEt_3)_2(R)X] + MeOH \rightleftarrows$ *cis*-$[Pt(PEt_3)_2(R)(MeOH)]^+ + X^-$ and of the Rate Constants for the Isomerization of the Solvento Complexes *cis*-$[Pt(PEt_3)_2(R)(MeOH)]^+$, As Obtained from Direct Measurements or from Mass Law Retardation Plots[a]

complex	10^5K_e[b]	10^5K_e[c]	10^3k_i,[c] s^{-1}	10^3k_i,[d] s^{-1}
R = Me; X = Cl	0.63 ± 0.02	8.4 ± 0.12	1.54 ± 0.1	6.76
R = Ph; X = Cl	0.51 ± 0.03	4.1 ± 0.1[e]	4.83 ± 0.03[e]	11.9
R = Ph; X = Br	0.15 ± 0.02	6.9 ± 0.1[e]	1.43 ± 0.1[e]	11.9
R = Ph; X = I		0.9 ± 0.2[e]	0.61 ± 0.4[e]	11.9

[a] At 30 °C. [b] From conductance data in Table VII. [c] From mass law retardation plots. [d] Direct measure. [e] From ref 24.

Table VII. Equivalent Conductance and Molar Concentrations of *cis*-$[Pt(PEt_3)_2(R)X]$ Complexes in Methanol[a]

R = Me; X = Cl		R = Ph; X = Cl		R = Ph; X = Br	
10^4C	Λ[b]	10^4C	Λ[b]	10^4C	Λ[b]
0.443	27.90	0.441	24.80	0.158	24.02
1.077	19.18	1.283	15.70	0.244	20.07
1.182	18.41	2.231	12.21	0.304	18.27
1.457	16.72	2.936	10.64	0.529	14.23
1.803	15.23	3.055	10.56	0.773	11.77
2.383	13.49	5.110	8.28	1.062	10.09
3.057	11.94	7.518	6.88	1.472	8.79
3.669	10.96	10.327	5.86	1.822	8.01
4.111	10.49	14.890	4.93	2.446	6.85
5.644	9.02			3.196	6.08
7.719	7.83			4.695	5.05
				5.68	4.61
$\Lambda_0 = 89 \pm 1$[c] $K = (6.3 \pm 0.2) \times 10^{-6}$		$\Lambda_0 = 86.4 \pm 2$[c] $K = (5.06 \pm 0.3) \times 10^{-6}$		$\Lambda_0 = 91 \pm 3$[c] $K = (1.5 \pm 0.2) \times 10^{-6}$	

[a] At 303.2 K. [b] In Ω^{-1} cm^{-1}. [c] In cm^2 Ω^{-1} $equiv^{-1}$.

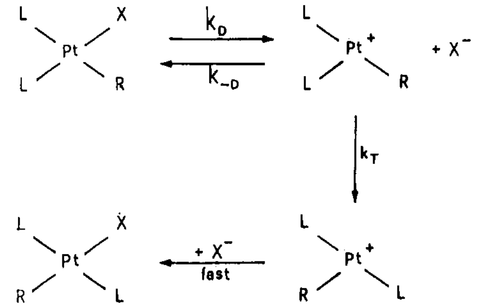
k_S/k_{-S}. From this rate expression it is possible to estimate values for k_T, rate constant for isomerization of the solvento intermediate, and for K_e, equilibrium constant of the solvolysis. The data derived from linear plots of k_i^{-1} vs $[X^-]$ or from nonlinear least-squares fit of k_i to $[X^-]$ values for the complexes *cis*-$[Pt(PEt_3)_2(R)X]$ (R = Me, X = Cl; R = Ph, X = Cl, Br, I) are collected in Table VI.

We have been able to perform an independent control of these rate and equilibrium constants. Indeed, k_T has been obtained directly from the rate of isomerization of *cis*-$[Pt(PEt_3)_2(R)(MeOH)]^+$. The equilibrium constants K_e were obtained by measuring the initial conductance of methanol solutions of *cis*-$[Pt(PEt_3)_2(R)X]$ complexes (Table VII), taking advantage of the slowness of their isomerization rate.

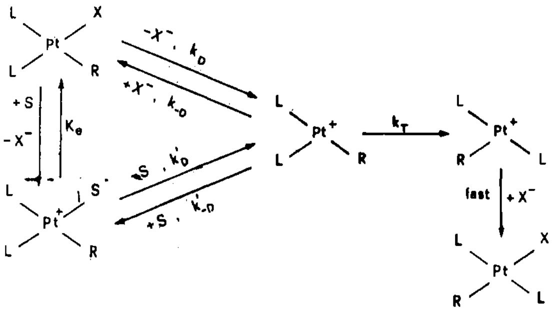
The two sets of data (Table VI) are hardly in agreement, giving unmistakable evidence against the preequilibrium mechanism. Such a reaction scheme for isomerization has been strongly supported by Kelm, van Eldik, et al., in a series of papers.[20–23] In one of them[22] they claim to obtain identical values for K_e from mass law retardation experiments and from conductance experiments, but unfortunately the actual conductance data from which K_e were calculated are not reported. If the values of K_e were in the range estimated from the mass law retardation data, at the low concentration of complex used for the kinetic runs ($<10^{-4}$ M), almost all the starting material should be converted to the solvento form.

Although the above findings rule out the preequilibrium mechanism, it is useful to add some other comment. The mechanism implies that the solvento complex $[Pt(PEt_3)_2(R)(MeOH)]^+$ is the *only* species undergoing isomerization but hardly explains how the geometrical change comes about. An intramolecular process through a tetrahedral intermediate can be ruled out on account of the high energy required, and even more, the proposal[21] of the intermediacy of a trigonal planar 3-coordinate species, since 14-electron ML_3 or ML_2X species are known to avoid the most symmetrical high-spin geometry in favor of Y- and T-shaped geometries of much lower energy.[7] As a consequence, effects on the rates produced by structural changes on the substrates or in the reaction medium cannot be explained or predicted.

Scheme III



Scheme IV



The mechanism originally proposed for uncatalyzed isomerization is shown in Scheme III and involves the dissociative loss of the X^- ligand and the conversion of two geometrically distinct T-shaped intermediates. The rate constant is given by eq 6, which

$$k_i = \frac{k_D}{1 + (k_{-D}/k_T)[X^-]} \tag{6}$$

simplifies to $k_i = k_D$ in the absence of added halide. Accordingly, the rates of isomerization are particularly sensitive to factors controlling bond dissociation as the nature of the leaving halide,[6] electron donation or withdrawal by substituents on the cis aromatic ring,[24] and the electrophilic ability of the solvent.[17] Except for the mesityl complex, large values of enthalpy and entropies of activation and positive volumes of activation are associated with isomerization (*cis-* to *trans*-$[Pt(PEt_3)_2(Ph)X]$ in MeOH, X = Cl, $\Delta V^{\ne} = +6.4 \pm 0.4$ cm^3 mol^{-1}; X = Br, $\Delta V^{\ne} = +5.2 \pm 0.3$ cm^3 mol^{-1}; X = I, $\Delta V^{\ne} = +7.2 \pm 0.8$ cm^3 mol^{-1}).[22]

It is now quite clear that such a reaction scheme, although consistent with all experimental findings, represents only a useful approximation. Indeed, in a strong dissociating medium such as methanol, it is necessary to take into account the solvolytic process and the possibility for *both* species in equilibrium to undergo isomerization through the dissociative loss of X or MeOH, respectively (Scheme IV). These processes (via k_D and k'_D) lead to a common T-shaped 3-coordinate intermediate, whose fate depends on the efficiency with which it is consumed by the reentry of either the halide ion (via k_{-D}) or the solvent molecule (via k'_{-D}) in competition with its conversion to the "trans-like" counterpart (k_T path). The rate expression derived for such a reaction scheme is

$$k_i = \frac{k_D[X^-] + k'_D K_e}{1 + (k'_{-D}/k_T)[S] + (k_{-D}/k_T)[X^-]} \, \frac{1}{K_e + [X^-]} \tag{7}$$

When no halide ion is present in solution, as in the isomerization of solvento species generated in situ, only the pathway via k'_D, k'_{-D} and k_T operates and (7) reduces to

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$$k_i = \frac{k'_D}{1 + (k'_{-D}/k_T)[S]} \tag{8}$$

The term $(k'_{-D}/k_T)[S]$ measures the retardation due to the capture of the intermediate by the bulk solvent. This effect decreases as the donor properties or the concentration of the solvent decrease, as we have seen in the isomerization of *cis*-[Pt(PEt$_3$)$_2$(Me)(MeOH)]$^+$ in methanol–diethyl ether mixtures. The value of the ratio k'_{-D}/k_T obtained from a nonlinear least-squares fit of the rate data in Table III to (8) is 2.075 mol^{-1}.

In the presence of added halide $[X^-] \gg K_e$ and eq 7 assumes the form

$$k_i = \frac{k_D[X^-] + k'_D K_e}{1 + (k'_{-D}/k_T)[S] + (k_{-D}/k_T)[X^-]} \frac{1}{[X^-]} \tag{9}$$

Replacing K_e by $k_D k'_{-D}/k'_D k_{-D}$, we get

$$k_i = \frac{k_D([X^-] + k'_{-D}/k_{-D})}{1 + (k'_{-D}/k_T)[S] + (k_{-D}/k_T)[X^-]} \frac{1}{[X^-]} \tag{10}$$

In order to agree with the empirical expression

$$k_i = \frac{a}{b + c[X^-]}$$

$[X^-] \gg k'_{-D}/k_{-D}$ and eq 7 simplifies to

$$k_i = \frac{k_D}{1 + (k'_{-D}/k_T)[S] + (k_{-D}/k_T)[X^-]} \tag{11}$$

This rate expression differs from that derived for Scheme III only by the inclusion of the retardation term due to the solvent. The value of the ratio k_{-D}/k_T, estimated from a nonlinear least-squares fit of the experimental data for the isomerization of *cis*-[Pt(PEt$_3$)$_2$(Me)Cl] in the presence of excess [Cl$^-$] (Table III) to (11) is 3.2×10^5 mol^{-1}.

If one relies on the values calculated for the ratios k'_{-D}/k_T and k_{-D}/k_T, then the ratio k_{-D}/k'_{-D} is $\simeq 10^5$. In other words, the efficiency with which X$^-$ captures the "cis-like" intermediate is at least 5 orders of magnitude higher than that of MeOH. Therefore, at concentrations of X$^-$ higher than 0.001 M, the only pathway which is active is that via k_D, k_{-D}, and k_T. Under these circumstances the original Scheme III and the relative rate law 6 are appropriate.

According to the above reasonings, the rate law that can be taken into account for isomerizations of *cis*-[Pt(PEt$_3$)$_2$(R)X] complexes in pure highly dissociating solvents has the form of (7), as derived from the general reaction scheme, Scheme IV. However, when the values of K_e are very low, a useful approximation is given by (11). This expression contains a constant term $(1 + (k'_{-D}/k_T)[S]$, which accounts for the trapping of the 3-coordinate intermediate by the bulk solvent. The estimate we have for this term (assuming it to be the same as that in MeOH and Et$_2$O) is $(1 + 2.07 \times 24.7) = 52$. Accordingly all the values of k_D and of the competition ratios k_{-D}/k_T estimated from (6) should be multiplied by this constant term. Such a correction is unnecessary when one compares the kinetic behavior of compounds of strictly similar structural properties.

To sum up, this work confirms that a key step in the mechanism of isomerization of monoorganophosphine complexes is the conversion of two T-shaped 3-coordinate 14-electron intermediates. The process is favored by factors promoting bond dissociation and inhibited by effective trapping of the first unsaturated intermediate. The anomalous behavior of *cis*-[Pt(PEt$_3$)$_2$(mes)Br] remains to be explained. We have already shown[6] that for this complex uncatalyzed isomerization and methanol solvolysis proceed at the same rate ($k_i = k_S = 0.19 \times 10^{-3}$ s^{-1}, at 30 °C) and with the same low ΔH^* (67 kJ mol^{-1}) and negative ΔS^* (−94 J K^{-1} mol^{-1}). Kelm, van Eldik, and Palmer[20] report a negative value for the volume of activation of both processes ($\Delta V^* = -14.1$ cm^3 mol^{-1}), consistent with an associative mechanism. We find here that *cis*-[Pt(PEt$_3$)$_2$(mes)(MeOH)]$^+$ isomerizes at a much higher rate ($k_i = 28.8 \times 10^{-3}$ s^{-1}, at 30 °C) with completely different activation parameters ($\Delta H^* = 106 \pm 4$ kJ mol^{-1}, $\Delta S^* = +75 \pm 8$ J K^{-1} mol^{-1}).

The only mechanism consistent with these findings, according to previous suggestions,[20] is the "solvolytic" one in Scheme II, which fits the condition $k_S \ll k_T$. The reason for this is less clear but must be related to the extremely crowded environment in this complex, which hinders the approach of the MeOH molecule either in its nucleophile part toward the metal or its electrophilic part toward the halide ion.

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Registry No. *cis*-[Pt(PEt$_3$)$_2$(Ph)(Me)], 111467-13-1; *cis*-[Pt(PEt$_3$)$_2$(mes)(Me)], 111410-22-1; *cis*-[Pt(PEt$_3$)$_2$(Me)$_2$], 22289-34-5; *cis*-[Pt(PEt$_3$)$_2$(Ph)Cl], 15702-92-8; *cis*-[Pt(PEt$_3$)$_2$(mes)Br], 22289-37-8; *cis*-[Pt(PEt$_3$)$_2$(Me)Cl], 22289-46-9; *cis*-[Pt(PEt$_3$)$_2$(Ph)Br], 15702-94-0; *cis*-[Pt(PEt$_3$)$_2$(Me)I], 111467-14-2; *cis*-[Pt(PEt$_3$)$_2$(Me)(MeOH)], 111467-15-3; *cis*-[Pt(PEt$_3$)$_2$(Ph)(MeOH)], 74280-92-5; *cis*-[Pt(PEt$_3$)$_2$(Me)(EtOH)], 111410-23-2; *cis*-[Pt(PEt$_3$)$_2$(Me)(PrOH)], 111410-24-3; *cis*-[Pt(PEt$_3$)$_2$(Me)(BuOH)], 111410-25-4; *cis*-[Pt(PEt$_3$)$_2$(Me)(*i*-PrOH)], 111410-26-5; *cis*-[Pt(PEt$_3$)$_2$(Me)(*t*-BuOH)], 111410-27-6.