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Uncatalyzed Cis–Trans Isomerization and Methanol Solvolysis of Arylbromobis(triethylphosphine)platinum(II) Complexes. A Different Role for Steric Hindrance in Dissociative and Associative Mechanisms

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Received September 15, 1975 AIC506809

The rates of the uncatalyzed cis–trans isomerization of the complexes *cis*-[Pt(PEt$_3$)$_2$(R)Br] (R = C_6H_5, *p*-MeC$_6$H$_4$, *o*-MeC$_6$H$_4$, *o*-EtC$_6$H$_4$, 2,4,6-Me$_3$C$_6$H$_2$) have been investigated in methanol at different temperatures and compared with the rates at which bromide is replaced by methanol. The isomerization rate is first order in the platinum complex and suffers mass law retardation by bromide ions. For all systems the isomeric equilibrium is well over to the trans form. Displacement of bromide by Y is consistent with the usual two-term rate law $k_{obsd} = k_1 + k_2[Y]$ although when $Y^- = I^-$ the contribution of k_2 is negligible. Ortho substitution in the phenyl ring only slightly affects the rates of isomerizations (k_i) but dramatically reduces the rates of attack by MeOH (k_1); $k_1 = k_i$ in the complex *cis*-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br]. This and other evidence indicates an associative mode of activation for solvolysis whereas isomerization proceeds via a dissociative asynchronous mechanism in which the rate-determining step is the breaking of a Pt–X bond to yield a three-coordinate "cis-like" intermediate. A comparison can be made of the relative importance of the two pathways in the substrates.

Introduction

There has been a great deal of interest in the last few years in the mechanism of cis–trans isomerization of platinum(II) and palladium(II) square-planar complexes, while less recent studies were limited to equilibrium[1] and photochemical[2] isomerization. This interest is in part aimed at integrating the mechanistic features of this conversion into the more general understanding of substitution reactions of these systems.[3]

Complexes of type *cis*- and *trans*-[PtL$_2$X$_2$] (X = halogen; L = tertiary phosphine, stibine, or arsine) are generally inert in solution but rapidly reach isomeric equilibrium in the presence of traces of the free ligand L. The mechanistic discussion of catalyzed isomerizations has centered around two alternative hypotheses. A reaction scheme proposed by Haake involves the association of L to give a distorted five-coordinate [L$_3$PtX$_2$] complex with a lifetime long enough to undergo a fluxional change which interconverts the positions of axial and equatorial ligands and enables isomerization.[4] Another mechanism, based originally on the knowledge of the stereochemically specific SN2 ligand displacement, implies the formation of an ionic intermediate of the type $[PtL_3X]^+X^-$ in a two-stage reaction, each step of which involves retention of configuration.[3] The consecutive displacement mechanism has found considerable support in a number of cases in which ionic intermediates were isolated as PF_6^- salts and it was possible to show by NMR that the exchange of the catalyst with the groups coordinated to the metal precedes isomerization, according to the known trans effect of the ligands.[5] Recent data aimed at disproving the double-displacement mechanism in the cis–trans isomerization of [Pt(PEt$_3$)$_2$Cl$_2$][6] were later shown to be fully consistent with it.[7] Cis–trans isomerization of the more labile palladium(II) complexes was shown to proceed through a consecutive displacement mechanism, which produces a fully dissociated ionic species when a strong base is used as catalyst,[8] or through a nonionic intermediate when displacement involves the solvent.[9] The emerging evidence is that the choice of the pathway for catalyzed cis–trans isomerization in these systems, pseudorotation of a five-coordinate intermediate or a displacement mechanism through an ionic or nonionic intermediate, depends on the metal, solvent, anion, steric hindrance of the ligands, basicity, and catalytic effects.

Some time ago we found that the complex *cis*-[Pt(PEt$_3$)$_2$(*o*-MeC$_6$H$_4$)Cl] spontaneously converts into its trans isomer in protic solvents.[10] Since isomerization suffers mass law retardation by chloride ion and its rate is very much less than that at which chloride is replaced by other nucleophiles, we proposed that the rate-determining step of isomerization involves the breaking of the bond between the metal and the chloride ion to yield a three-coordinate intermediate. This conclusion was a surprising one, in that, at that time, there was much evidence of five-coordinate platinum(II) either as discrete compounds or as reaction intermediates,[11] while the existence of three-coordinate species had not been postulated.

We report herein a detailed study of the effect of increasing steric hindrance on the rates of spontaneous cis–trans isomerization of [Pt(PEt$_3$)$_2$(R)Br] complexes in methanol and on the rates of bromide substitution by the solvent. It will be shown that a dissociative path, which represents a negligible contribution to the reactivity of unhindered complexes, becomes the rate-determining step of both isomerization and substitution in the complex [Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br]. A preliminary communication has appeared.[12]

Experimental Section

Preparation of Compounds. ***cis*-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br]** and ***cis*-[Pt(PEt$_3$)$_2$(R)Cl] (R = Ph, *o*-MeC$_6$H$_4$, and *p*-MeC$_6$H$_4$)** were prepared using the general procedures described by Chatt and Shaw.[13] These last species were used as starting materials to obtain the corresponding cis bromo derivatives by metathetical exchange with lithium bromide in acetone. ***trans*-[Pt(PEt$_3$)$_2$(R)Br]** complexes were obtained from their cis isomers using the method of Basolo et al.[14]

The following new compounds were prepared.

***cis*-[Pt(*o*-EtC$_6$H$_4$)$_2$(PEt$_3$)$_2$].** To a suspension of 2 g of *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] in dry benzene (30 ml) was added dropwise under nitrogen an ethereal solution of *o*-ethylphenyllithium (20% excess). After 30 min of stirring at room temperature, benzene and water were added. The crude pale yellow product obtained by evaporation of the organic layer was washed with small portions of cold petroleum ether (bp 40–70 °C). The residue on crystallization from the same solvent gave 1.43 g of white needles (mp 159–161 °C). Anal. Calcd for $C_{28}H_{48}P_2Pt$: C, 52.49; H, 7.40. Found: C, 52.63; H, 7.57.

***cis*-[PtCl(*o*-EtC$_6$H$_4$)(PEt$_3$)$_2$].** *cis*-Bis(triethylphosphine)bis(*o*-ethylphenyl)platinum (1.0 g) in toluene was treated with a stoichiometric quantity of dry HCl in toluene. After 2 h the solution was evaporated to dryness. Recrystallization from petroleum ether (bp 40–70 °C) gave 0.55 g as white needles (mp 139–142 °C). Some unreacted starting material was found in the mother liquor. Anal. Calcd for $C_{20}H_{39}ClP_2Pt$: C, 42.00; H, 6.87; Cl, 6.19. Found: C, 41.91; H, 7.01, Cl, 6.52.

***cis*-[PtBr(*o*-EtC$_6$H$_4$)(PEt$_3$)$_2$]** was prepared in an almost quantitative yield by allowing 0.25 g of the chloride to react with lithium bromide (0.35 g) under reflux for 15 min in acetone. After evaporation of the solvent, the residue was washed with water, dried, and crystallized from a benzene–petroleum ether mixture (mp 145–147 °C). Anal. Calcd for $C_{20}H_{39}BrP_2Pt$: C, 38.97; H, 6.38; Br, 12.96. Found: C, 38.80; H, 6.40; Br, 13.33.

***trans*-[PtBr(*o*-EtC$_6$H$_4$)(PEt$_3$)$_2$].** A solution of *cis*-[PtCl(*o*-EtC$_6$H$_4$)(PEt$_3$)$_2$] (0.25 g) in methanol was treated with a stoichiometric quantity of silver nitrate in methanol–water. The mixture was shaken for 1 h and then the silver chloride was filtered off and lithium bromide (0.1 g) was added to the filtrate. After 20 min of heating the solvent was evaporated and water added. The residue was dried and recrystallized from petroleum ether. Anal. Calcd for $C_{20}H_{39}BrP_2Pt$: C, 38.97; H, 6.38; Br, 12.96. Found: C, 38.85; H, 6.43; Br, 13.26.

All compounds gave satisfactory elementary analyses and their stereochemistry was established by Goggin and Goodfellow's method.[15] The ir spectra (measured on Nujol mulls with a Perkin-Elmer 577 spectrophotometer) showed two Pt–P stretching frequencies in the region between 410 and 440 cm^{-1} for the cis compounds and only one for the trans.

Kinetics. All reactions were followed spectrophotometrically but the technique used depended upon the rate.

The isomerization reactions were carried out in a silica cell in the thermostated cell compartment of a double-beam Optica CF 4 spectrophotometer, where the temperature remained constant to ±0.05 °C. The solvent was brought to reaction temperature in the spectrophotometer and the reaction was started by adding the complex and stirring the solution rapidly. Spectra were scanned at appropriate times and first-order rate constants k_i (s^{-1}) were obtained from the usual semilog plots, using the wavelength at which the absorbance change was largest.

The same standard repetitive scanning technique was used to follow the nucleophilic substitution reactions of the complex *cis*-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br], which were also started by dissolving the solid substrate in the reagent solution. Other faster substitution reactions were followed at a single wavelength using a Beckman DU spectrophotometer, equipped with a Saitron 301 photometer and a Servogor S recording potentiometer. The reaction mixture was obtained by adding with a microsyringe 0.1 ml of complex solution to 3 ml of thermostated reagent solution. The cis compound was dissolved at −15 °C and the solution was stored at this temperature, in order to prevent isomerization in the stock solution. Alternatively, isomerization was blocked by dissolving the substrate in 0.01 M lithium bromide. Several experiments were treated by both procedures and the calculated values of the rate constants always agreed within experimental error.

Fast reactions were followed using a Durrum D 110 stopped-flow spectrophotometer equipped with thermostated glass syringes and a Teflon mixing chamber. Transmittance changes, at a selected wavelength, were displayed on a storage oscilloscope and traces were photographed with a Polaroid camera. In these reactions isomerization was prevented by adding lithium bromide to the solution of the cis starting material. Lithium perchlorate was present in the solution of the complex as well as that of the reagent in order to ensure that the ionic strength of the two solutions was the same before mixing.

A large excess of reagent was always used to provide pseudo-first-order conditions and the pseudo-first-order rate constants k_{obsd} (s^{-1}) were calculated from the gradients of the usual first-order plots. Activation parameters were obtained from linear least-squares analyses of Eyring plots.

Results

Rate Studies. (a) Spontaneous Isomerization. The species *cis*-[Pt(PEt$_3$)$_2$(R)Br] start to isomerize as soon as the solid compounds are dissolved in methanol. The spectral changes in the uv region shown clean isosbestic points, indicating that the two isomers are the only absorbing species in solution. In all cases the equilibria largely favor the trans form; the final uv spectra are virtually identical with those of independently prepared solutions of trans isomers. Qualitative layer chromatography tests on the final mixtures as well as ir spectra of the isolated reaction products showed the presence of traces of cis isomer, but no attempts were made to measure the equilibrium constants.

The isomerization followed a first-order rate law. The specific rate constants k_i at various temperatures are collected in Table I. The rate of isomerization is greatly reduced by the addition of very small amounts of bromide ion as shown by the values of the first-order rate constants in Table II. Since the rate of isomerization increases on increasing the ionic strength, the kinetic runs were carried out by keeping the ionic strength constant at 0.01 M with LiClO$_4$. (Solvent effects and salt effects on the rate of isomerization will be discussed in detail in a later paper.) Plots of k_i^{-1} for these experiments vs. [Br$^-$] (Figure 1) give straight lines with finite intercepts, which are identical with the k_i^{-1} values obtained in absence of bromide.

Table I. Temperature Dependence of the Rate Constants for the Isomerization Reactions[a] in Methanol

$$cis\text{-}[Pt(PEt_3)_2(R)Br] \underset{k_r}{\overset{k_f}{\rightleftharpoons}} trans\text{-}[Pt(PEt_3)_2(R)Br]$$

	10^3k_i, s^{-1}				
Temp, °C	R = Ph	R = *p*-MeC$_6$H$_4$	R = *o*-MeC$_6$H$_4$	R = *o*-EtC$_6$H$_4$	R = 2,4,6-Me$_3$C$_6$H$_2$
25	0.63	1.45	0.37	0.33	0.10
30	1.07	2.34	0.72	0.55	0.17
35	1.91	4.38	1.33	1.07	0.27
40	3.40	7.01	2.52	2.22	0.40
45	6.17	12.0	4.92	4.28	0.60

[a] 5.0×10^{-5} M complex; $k_i = k_f + k_r$.

Table II. Effect of Lithium Bromide on the Rate of Cis → Trans Isomerization of the Complexes [Pt(PEt$_3$)$_2$(R)Br] in Methanol at 30 °C (μ = 0.01 M (LiClO$_4$); 5.0×10^{-5} M Complex)

R	10^4[Br$^-$], M	10^4k_{obsd}, s^{-1}	R	10^4[Br$^-$], M	10^4k_{obsd}, s^{-1}
Ph	0.0	13.8	*o*-MeC$_6$H$_4$	0.0	6.95
	0.8	7.23		0.6	3.91
	2.0	3.62		0.8	3.34
	4.0	2.05		2.0	1.74
	8.0	1.17		4.0	0.96
	12.0	0.78		8.0	0.58
				12.0	0.38
p-MeC$_6$H$_4$	0.0	38.4			
	1.0	12.6	*o*-EtC$_6$H$_4$	0.0	9.79
	2.0	7.25		1.0	3.55
	4.0	3.71		2.0	1.92
	6.0	2.42		4.0	1.09
	8.0	2.03		6.0	0.77
	10.0	1.45	2,4,6-Me$_3$C$_6$H$_2$	0.0	2.13
	20.0	0.76		2.0	1.05
	30.0	0.58		4.0	0.69
				6.0	0.53
				8.0	0.43

(b) Nucleophilic Substitution. The kinetics of the reactions

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

were examined at iodide concentrations ranging from 1.0×10^{-3} to 10^{-1} M. The final spectra were identical with those of the authentic *cis*-[Pt(PEt$_3$)$_2$(R)I] complexes. Unlike the usual behavior of platinum(II) complexes toward nucleophilic displacement, the entry of the iodide occurs at a rate independent of [I$^-$]. The values of k_1 at different temperatures listed in Table III are the mean of a number of runs carried out with different iodide concentrations. A definite second-order contribution is exhibited only by reagents like thiocyanide and cyanide which have nucleophilic reactivities greater than iodide. In these cases the variation of the pseudo-first-order rate constants with reagent concentration (Figure 2) is consistent with the two-term rate law $k_{obsd} = k_1 + k_2[Y]$. Unlike k_i, k_1 is not significantly affected by large variations in bromide concentrations, as shown by the values of the pseudo-first-order rate constants in Table IV.

Discussion

Spontaneous Isomerization. Dissociative Mechanism. Mass law retardation of the isomerization by bromide suggests that the rate-determining step must involve the reversible release

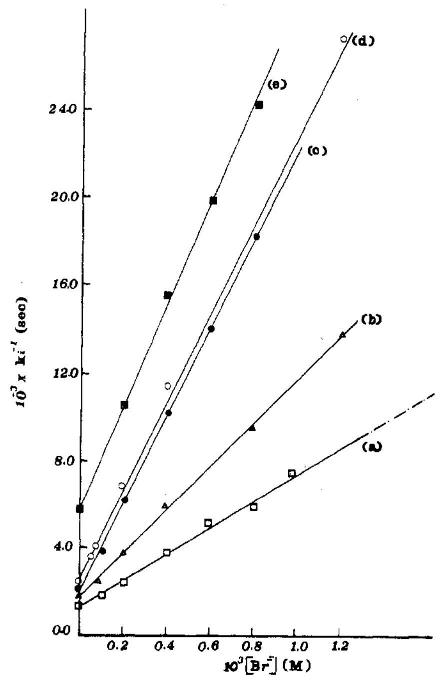


Figure 1. Changes of cis-trans isomerization rates of *cis*-$[Pt(PEt_3)_2(R)Br]$ with lithium bromide concentration in methanol at 30 °C: (a) R = *p*-MeC_6H_4, $k_{-D}/k_T = 2.78 \times 10^4$; (b) R = phenyl, $k_{-D}/k_T = 1.42 \times 10^4$; (c) R = *o*-$EtC_6H_4$, $k_{-D}/k_T = 2.08 \times 10^4$; (d) R = *o*-$MeC_6H_4$, $k_{-D}/k_T = 1.28 \times 10^4$; (e) R = 2,4,6-$Me_3C_6H_2$, $k_{-D}/k_T = 0.43 \times 10^4$.

Table III. Temperature Dependence of the Rates of Bromide Displacement by Iodide from the Complexes *cis*-$[Pt(PEt_3)_2(R)Br]$ ($\mu = 0.1$ M ($LiNO_3$); 1.0×10^{-4} M Complex)

R	Temp, °C	k_1, s^{-1}	R	Temp, °C	k_1, s^{-1}
Ph	15	2.00	*o*-MeC_6H_4	15	1.79×10^{-2}
	30	6.00		30	5.44×10^{-2}
	40	12.20		40	11.0×10^{-2}
p-MeC_6H_4	20	2.24	*o*-EtC_6H_4	15	0.52×10^{-2}
	30	4.28		30	1.62×10^{-2}
	40	8.35		40	3.51×10^{-2}
			2,4,6-$Me_3C_6H_2$	25	1.33×10^{-4}
				30	1.94×10^{-4}
				35	3.08×10^{-4}
				40	5.07×10^{-4}
				45	7.47×10^{-4}

Table IV. Effect of Varying $[Br^-]$ on the Rate of Bromide Substitution from *cis*-$[PtBr(o\text{-}MeC_6H_4)(PEt_3)_2]$ by 0.1 M Iodide at 17 °C in MeOH

$[Br^-]$, M	10^2k_{obsd}, s^{-1}	$[Br^-]$, M	10^2k_{obsd}, s^{-1}
0.0	2.06	0.008	2.10
0.004	2.11	0.010	2.11
0.006	2.11	0.020	2.05

of bromide. The asynchronous mechanism already proposed[10] involves a dissociative path in which the breaking of the bond between the metal and the halide ion yields a labile three-coordinate "cis-like" intermediate. This is then converted to its "trans-like" structure which eventually takes up halide ion to give the trans isomerization product. (See Scheme I.) Because the isomeric equilibrium is well over to trans form, the rate constants k_{-3} and k_{-T} can be ignored. Steady-state treatment of species I leads to the expression for the isomerization rate constant

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

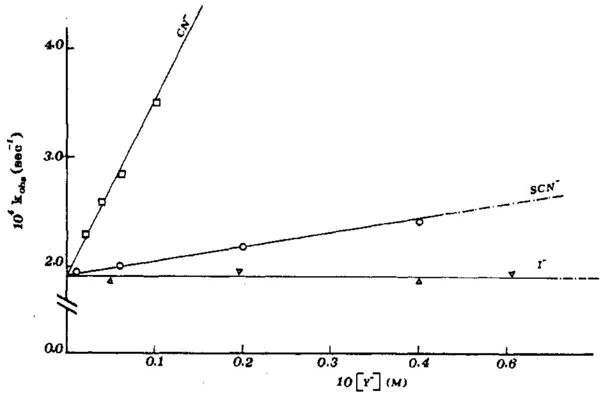
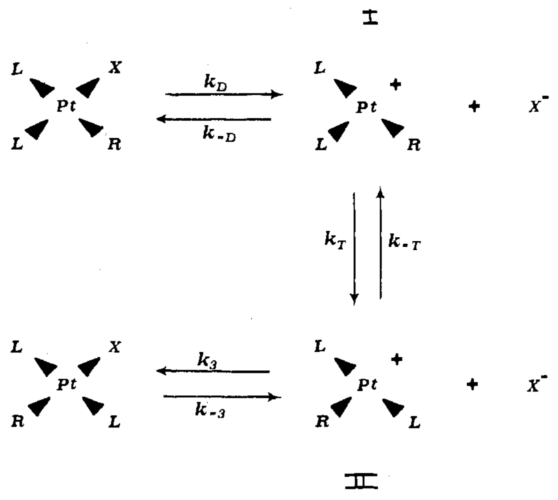
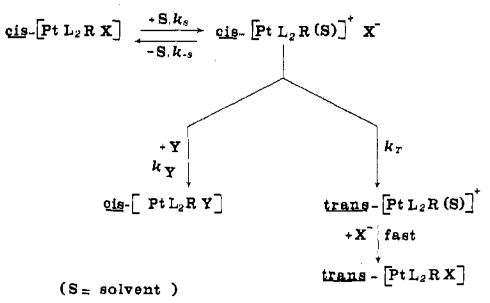


Figure 2. Plot of k_{obsd} vs. anion concentration in reactions of *cis*-$[Pt(PEt_3)_2(2,4,6\text{-}Me_3C_6H_2)Br]$ with I^-, SCN^-, and CN^- in methanol at 30 °C.

Scheme I



Scheme II



which in the form

$$k_i^{-1} = k_D^{-1} + (k_{-D}/k_D k_T)[X^-] \qquad (2)$$

accounts for linear plots of k_i^{-1} against $[Br^-]$. The rate of metal–halide bond breaking is the isomerization rate when $[X^-] = 0$.

Bimolecular attack by solvent on the substrate involves also reversible release of bromide and formation of a solvato complex which might be a common intermediate for either substitution or isomerization. (See Scheme II.)

The rate law for isomerization would then be

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

while the solvolytic rate law for substitution would be

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

Table V. Comparison of Rate Constants at 30 °C and Activation Parameters for Cis → Trans Isomerization (k_i, $\Delta H_i^\ddagger$, $\Delta S_i^\ddagger$) and Bromide Displacement by MeOH (k_1, $\Delta H_1^\ddagger$ $\Delta S_1^\ddagger$) for the Complexes *cis*-[Pt(PEt$_3$)$_2$(R)Br] in Methanol

R	$10^3 k_i$, s^{-1}	$10^3 k_1$, s^{-1}	$\Delta H_i^\ddagger$, kcal mol^{-1}	$\Delta H_1^\ddagger$, kcal mol^{-1}	$\Delta S_i^\ddagger$, cal K^{-1} mol^{-1}	$\Delta S_1^\ddagger$, cal K^{-1} mol^{-1}
Ph	1.07	6000	21.0	12.3	−3.0	−14.2
p-MeC$_6$H$_4$	2.34	4280	19.5	11.4	−6.2	−18.0
o-MeC$_6$H$_4$	0.72	54.4	23.6	12.4	+5.0	−23.4
o-EtC$_6$H$_4$	0.55	16.2	24.0	13.0	+5.7	−23.6
2,4,6-Me$_3$C$_6$H$_2$	0.19[a]	0.19	16.1	16.0	−22.6	−22.6

[a] At $\mu = 0.1$ M (LiNO$_3$).

In the absence of added halide ion (when no mass retardation effects are observed in either path) this mechanism would lead to the conclusion that $k_i = k_1$, in sharp contrast to what is found. A comparison of the data in Table V shows that in most cases the rate of solvolysis is much faster than isomerization.

Effect of Increasing the Bulkiness of R. (a) Isomerization. The data in Table V show that the rate of isomerization is almost insensitive to steric crowding produced by ortho alkyl substitution on the aromatic ring; k_i varies by less than a factor of 6. This is consistent with a dissociative asynchronous mechanism in which the breaking of the Pt–X bond is the most important factor determining the rate and the remaining coordinate ligands essentially keep their original positions around the central metal in the "cis-like" structure of the three-coordinate cationic intermediate. The lack of a significant steric acceleration in the rate of the dissociative process is due to the fact that the loss of the leaving group is not accompanied by an expansion and rearrangement of the remaining ancillary ligands to relieve steric strain in a transition state of reduced coordination number. The large $\Delta H^\ddagger$ and $\Delta S^\ddagger$ associated with isomerization (Table V) agree with a dissociative mechanism.[16]

It is interesting to note that rate and activation data for isomerization of *cis*-[Pt(PEt$_3$)$_2$(*p*-MeC$_6$H$_4$)Br] indicate that electron donation accelerates the loss of the halide ion. Preliminary results on an extensive series of para-substituted aryl complexes confirm that the effect of electron-releasing groups is to increase k_i while electron-withdrawing groups have the opposite effect.

(b) Solvolysis. The occurrence of a reagent-independent term k_1 in the rate law for substitution of X by Y implies a reaction path in which a labile intermediate is formed which rapidly takes up the nucleophile Y to form the product. There has been much debate on the intimate nature of this pathway as to whether a dissociative mechanism or an associative solvolysis or even a concerted process was involved. Extensive kinetic studies on such systems clearly reveal common mechanistic features for both the reagent-dependent and -independent pathways and there is now little doubt as to the associative nature of the solvent-assisted path.

A clear-cut example of associative solvolysis has been given by Gray in competition experiments on the intermediate [Pt(dien)H$_2$O]$^{2+}$ (dien = 1,5-diamino-3-azapentane) which is formed in the solvent path of halide displacement from [Pt(dien)I]$^+$.[17]

By way of contrast a fuller understanding of the role of the solvent is still needed in cases where steric crowding is too great to permit the entrance of solvent molecules with large donor atoms[18] or when the trans influence of the ligand trans to X is so high as to produce a considerable ground-state weakening and lengthening of the Pt–X bond.[19]

Bearing this in mind, the fact that $k_2 = 0$ in the bromide displacement by iodide from *cis*-[Pt(PEt$_3$)$_2$(R)Br] cannot be taken as evidence of a changeover in the normal associative mode of reaction but as an indication of high intrinsic reactivity and low discriminating ability of these substrates.

Basolo pioneered in the use of ortho methyl substitutions to see steric effects on the transition state. The fact that the main decrease in rate occurs when the aryl ligand is cis to the leaving group has been taken as evidence for a trigonal-bipyramidal transition state, in which the trans ligand and the entering and leaving groups are in the trigonal plane and the two ex-cis ligands occupy the apical positions.[14,20] Strain effects on the rate of solvolysis of the complexes *cis*-[Pt(PEt$_3$)$_2$(R)Br] are in the direction expected for an associative mechanism. The rate constants for bimolecular attack by methanol are dramatically reduced in the order Ph $\simeq$ *p*-MeC$_6$H$_4$ $\gg$ *o*-MeC$_6$H$_6$ > *o*-EtC$_6$H$_4$ > 2,4,6-Me$_3$C$_6$H$_2$ and approach k_i values which in contrast are not affected significantly.

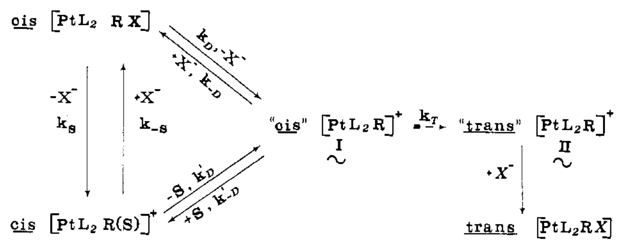
Bimolecular attack on the complex *cis*-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br] is made energetically unfavorable by congestion produced by the axial aryl ligand which extends two ortho methyl groups well into the equatorial plane. Isomerization and substitution proceed at the same rate ($k_i = k_1$) and only the dissociative pathway controls both processes. It is interesting to note that this complex appears to be nearly as crowded as the so-called "pseudooctahedral" complexes of the type [M(Et$_4$dien)X]$^+$ (M = Pt, Pd; (Et$_4$dien = *N,N,N',N'*-tetraethyl-1,5-diamino-3-azapentane) in which the chloride ion substitution reactions in methanol were shown by Roulet and Gray to proceed via an associative solvolysis pathway.[21] A likely explanation could be that either the bulky ancillary ligands in *cis*-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br] create a more effective and specific destabilization of the five-coordinate transition-state structure or, alternatively, the phosphorus atom produces a greater ground-state weakening of M–X bond than nitrogen, favoring the dissociative path, or else that both factors are important.

The low values of enthalpy of activation (Table V) and the largely negative entropies associated with the entry of methanol on the complexes *cis*-[Pt(PEt$_3$)$_2$(R)Br] fit well in the simplified picture of an associative mechanism in which bond making by the entering group results in the formation of a compact transition state.[22] Because k_i is characterized by a much less negative or even positive entropy of activation and a larger enthalpy of activation, we would therefore have expected for the mesityl complex, where $k_1 = k_i$, a higher $\Delta H^\ddagger$ and a high, even positive $\Delta S^\ddagger$. Although we are not sure why the prediction fails, it is likely that the low $\Delta H^\ddagger$ can be related to the inductive effect of the three substituted methyl groups on the coordinated mesityl ring. The negative entropy of activation could be due to a change in the balance of solvent molecules associated around the crowded ground state and transition states.

Finally it should be noted that the comparison of the data in Table V, which relate to two different modes of activation for release of bromide from the complexes *cis*-[Pt(PEt$_3$)$_2$(R)Br], show unambiguously that the associative mechanism remains the favorable pathway of square-planar platinum(II) complexes and the dissociative mechanism, while being obviously present, makes only a negligible contribution to the reactivity in unhindered systems.

Three-Coordinate Species. Scheme I involves the presence in the reaction profile of two minima, corresponding to an unusual T form that can easily interconvert. Three lines of evidence indicate a T form for these intermediates: (1) a single intermediate, which had the ability to recombine with the halide ion in alternative ways, one leading to the cis and the other to the trans product, could not account for halide ion mass law retardation; (2) the low sensitivity of isomerization

Scheme III



rate to steric crowding suggests that the breaking of the platinum–halide bond in the slow step is not significantly assisted by distortion of the remaining groups coordinated to the metal; (3) in the substitution reactions of bromide by iodide on *cis*-[PtBr(2,4,6-$Me_3C_6H_2$)(PEt_3)$_2$], in which steric restrictions do not allow associative solvolysis to take place, substitution proceeds through the dissociative k_D pathway and the only product is the cis iodo derivative. The fact that the substitution proceeds with complete retention of the original geometrical configuration indicates that the iodide ion scavenges the three-coordinate "cis-like" intermediate before its conversion to the "trans-like" structure. Strong support for this comes from the values of the ratios k_{-D}/k_T that represent the efficiency of the chloride ion in capturing the reactive intermediate I in competition with the process leading from I to II. These values can be easily calculated from the ratios of slopes to intercepts in Figure 2. It appears that the activation free energy for conversion of I to II is much higher than for the halide reentering to I. The circumstance that the ratios k_{-D}/k_T keep nearly constant along the series of complexes could be interpreted as an indication that the extent of steric hindrance in I either does not influence or influences to the same degree the processes occurring through pathways k_{-D} and k_T.

Participation of the solvent in competing for the reactive intermediate I can be accounted for by Scheme III, where k'_{-D} is the rate constant for the attack of the solvent on I. Assuming fast reentry of halide ion on the solvento complex [$PtL_2R(S)$]$^+$, this mechanism would lead to a rate law of the form

$$k_i = \frac{k_T k_D}{k_T + k_{-D}[X^-] + k'_{-D}} \tag{5}$$

Substitution reactions on *cis*-[Pt(PEt_3)$_2$(2,4,6-$Me_3C_6H_2$)Br] indicate that associative solvolysis is unactive and the iodide ion captures the intermediate I as soon as it is formed via k_D so that $k_I = k_D$. Because isomerization in the absence of added halide ([X^-] = 0) and substitution proceed at the same rate ($k_I = k_i$), it is clear that, at least in this case, the contribution of the pathway via k'_{-D} is negligible and conversion of I into II precedes the possible attack by solvent.

Three-coordinate Pt(II) species have recently been invoked in the thermal decomposition of [Pt(PPh_3)$_2$(n-C_4H_9)$_2$],[23] in the mechanism of olefin insertion into a platinum–hydrogen bond,[24] in the kinetics of the conversion of methyl carbonyl into acetyl derivatives,[25] and in the reverse reaction, viz., the alkyl migration from carbon monoxide to platinum.[26]

Finally, it should be noted that, all of these three-coordinate species contradict Tolman's 16–18 electron rule,[27] although the use of formal valence-state terminology is questionable when the ligands contain aryl groups which may be capable of donating additional electrons to the metal atom.

Acknowledgment. We wish to thank Professor Martin L. Tobe of the University College of London for helpful and stimulating discussions and the italian CNR for financial support.

Registry No. *cis*-[Pt(PEt_3)$_2$(Ph)Br], 15702-94-0; *cis*-[Pt(PEt_3)$_2$(p-MeC_6H_4)Br], 56531-35-2; *cis*-[Pt(PEt_3)$_2$(o-MeC_6H_4)Br], 56531-05-6; *cis*-[Pt(PEt_3)$_2$(o-EtC_6H_4)Br], 56531-34-1; *trans*-[Pt(PEt_3)$_2$(o-EtC_6H_4)Br], 58267-06-4; *cis*-[Pt(PEt_3)$_2$(2,4,6-$Me_3C_6H_2$)Br], 22289-37-8; Br^-, 24959-67-9; I^-, 20461-54-5; SCN^-, 302-04-5; CN^-, 57-12-5; bromine, 7726-95-6; *cis*-[Pt(o-EtC_6H_4)$_2$(PEt_3)$_2$], 58220-16-9; *cis*-[PtCl(o-EtC_6H_4)(PEt_3)$_2$], 58220-17-0; *cis*-[Pt(PEt_3)$_2Cl_2$], 15692-07-6; o-ethylphenyllithium, 41285-21-6.

Supplementary Material Available: Listing of specific kinetic data used to estimate values in Table V (4 pages). Ordering information is given on any current masthead page.

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