63230-72-8; allyloxycyclooctatetraene, 63197-34-2; 2-propen-1-ol, 107-18-6; bromocyclooctatetraene, 7567-22-8; methyl iodide, 74-88-4; *tert*-butyllithium, 594-19-4; *n*-butyllithium, 109-72-8; methyllithium, 917-54-4; phenyllithium, 591-51-5; vinyllithium, 917-57-7; allyllithium, 3052-45-7.

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Preparative and Kinetic Study on the Mechanisms of Isomerization of Square-Planar Complexes. Kinetic Evidence for Pseudorotation of a Five-Coordinate Intermediate

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It was found that, on addition of a stoichiometric or excess amount of L to PtX$_2$L$_2$, PtXL$_3^+$ is formed in polar solvents and PtX$_2$L$_3$ (X = Cl, Br, I; L = PMe$_2$Ph, PEt$_3$) in nonpolar solvents. In conjunction with this, either no or a very slow isomerization occurs in polar solvents, while a very fast isomerization proceeds in nonpolar solvents. A kinetic study of the iodide-catalyzed cis to trans isomerization of PtI$_2$(PEt$_3$)$_2$ showed that pseudorotation of a five-coordinate intermediate is most probably the isomerization pathway. Some further arguments are presented in support of this mechanism for the phosphine-catalyzed as well as uncatalyzed MX$_2$L$_2$, MR$_2$L$_2$, and AuR$_2$R'L (R = alkyl or aryl) isomerizations. However, the consecutive displacement mechanism most probably operates for MXRL$_2$ and MX$_2$X'$_2$ (X' = halide, amine, or water) systems.

Introduction

Catalyzed isomerization of platinum(II) and palladium(II) phosphine–, arsine–, stibine–, and amine–halo complexes (MX$_2$L$_2$) is well-known. Two of the previously proposed mechanisms can accommodate all of the observations to date. Basolo and Pearson[1] postulated a consecutive displacement mechanism that does not contradict the stereospecific nature of substitution in square-planar complexes:

$$cis\text{-}MX_2L_2 \overset{L'}{\rightleftharpoons} MXL'L_2 + X^- \overset{-L}{\rightleftharpoons} trans\text{-}MX_2L'L \qquad (1)$$
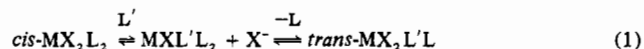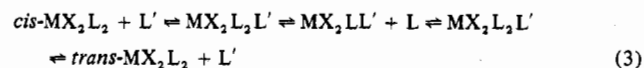
Haake et al.[2] presented some data from which they concluded that the phosphines L and L' do not mix during isomerization. They therefore postulated "a distorted penta-coordinate state in which L' occupies a unique position. This distorted state must be able to undergo fluxional change which interconverts the positions of L and X and, therefore enables isomerization" to occur:

$$cis\text{-}MX_2L_2 \overset{L'}{\rightleftharpoons} MX_2L_2L' \overset{-L'}{\rightleftharpoons} trans\text{-}MX_2L_2 \qquad (2)$$
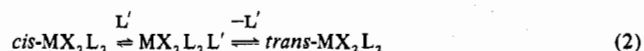
However, Cooper and Powell[3] later did some NMR studies from which they concluded that Haake's conclusion was erroneous, though a pseudorotation mechanism could not be discounted from their observations. The latter experiments were repeated and different results were found which will be

discussed in the section on NMR studies.

Recently Redfield and Nelson[4] showed that MX$_2$LL' can be isolated in certain cases and is formed from mixtures of MX$_2$L$_2$ and MX$_2$L$_2'$. Their data implied that there can be phosphine mixing, and therefore no unique M–L' bond need exist. They suggested that both mechanisms 1 and 2 operate, depending on choice of solvent and ligand. A third mechanism was also suggested,[4] namely, consecutive displacement of a neutral ligand by a neutral ligand:

$$cis\text{-}MX_2L_2 + L' \rightleftharpoons MX_2L_2L' \rightleftharpoons MX_2LL' + L \rightleftharpoons MX_2L_2L'$$
$$\rightleftharpoons trans\text{-}MX_2L_2 + L' \qquad (3)$$

Because of the very stereospecific nature of the square-planar substitution reactions it is however very doubtful whether isomerization will be achieved by this mechanism.

Two further mechanisms can be proposed for *cis–trans* isomerization. First, one can conceive that an equilibrium between the tetrahedral and square-planar structures can result in isomerization, but this mechanism has been found to be symmetry forbidden.[5] Second, isomerization can be effected by an equilibrium between a square-planar and trigonal structure, but such a dissociative step is violating Tolman's 16–18 electron rule[29] and has never been found in Pt(II) and Pd(II) square-planar substitutions to date.[1] Nevertheless, this mechanism has been postulated for some uncatalyzed isomerizations[24] and will be discussed later.

Quite a few NMR and kinetic studies have been done on isomerization systems, but neither of the mechanisms 1 and 2 could be discounted in any case reported. To further complicate the system, both intermediates MX_2L_2L' and $MXL_2L'^+$ have been isolated in various cases.[6]

This present study investigated the conditions required for intermediate ($PtXL_3^+$ and PtX_2L_3 (X = Cl, Br, I; L = PMe_2Ph, PEt_3)) formation, and finally kinetic studies of the phosphine-catalyzed isomerization

$$cis\text{-}PtI_2L_2 + L \xrightarrow[\text{(n-Bu)}_4 \text{NI, } C_6H_6]{\text{NaI, } CH_3 \text{ OH}} trans\text{-}PtI_2L_2 + L \qquad (4)$$
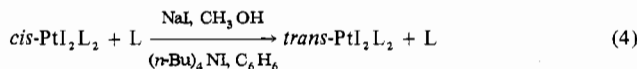
(L = PEt_3, PMe_2Ph) in both methanol and benzene and the iodide-catalyzed isomerization

$$cis\text{-}PtI_2(PEt_3)_2 + I^- \xrightarrow{\text{MeOH}} trans\text{-}PtI_2(PEt_3)_2 + I^- \qquad (5)$$
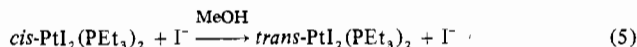
were done. For reaction 5 it was possible to distinguish kinetically between the proposed mechanisms 1 and 2. These results are now presented here.

Experimental Section

Preparation of Complexes. *cis*-**Dichlorobis(dimethylphenylphosphine)platinum(II) (an Improved Preparation).**[7] A solution of PMe_2Ph (1 mL, 2.1 equiv) in ethanol (15 mL) was added dropwise with stirring to a solution of K_2PtCl_4 (1.5 g) in water (25 mL). The resultant brown precipitate was filtered off after 15–20 min, washed with water, and then recrystallized from ethanol–charcoal mixtures to give *cis*-$PtCl_2(PMe_2Ph)_2$ as white prisms (yield 70%). Anal. Calcd for $PtCl_2(PMe_2Ph)_2$: C, 35.4; H, 4.1; Cl, 13.1. Found: C, 35.3; H, 4.1; Cl, 12.9.

trans-**Dichlorobis(triethylphosphine)platinum(II) (an Improved Preparation).** This preparation was carried out under nitrogen atmosphere. A solution of PEt_3 (10 mL) in ethanol (50 mL) was added dropwise with stirring to a K_2PtCl_4 (10 g) solution in water (100 mL) and refluxed for 5 min. A better yield is obtained when the reflux apparatus is sealed under N_2 rather than when N_2 is passed through the system. Stirring was continued until the solution cooled to room temperature. The resultant yellow precipitate was filtered off, dissolved in ether, and filtered to remove the insoluble white cis species. The ether solution was evaporated under reduced pressure and the yellow *trans*-$PtCl_2(PEt_3)_2$ recrystallized from ethanol (yield 60%). Anal. Calcd for $PtCl_2(PEt_3)_2$: C, 28.7; H, 6.0; Cl, 14.1. Found: C, 29.0; H, 6.3; Cl, 13.9.

The following complexes were all prepared according to literature methods: *cis*-$PtX_2(PMe_2Ph)_2$ (X = Br, I),[7] *trans*-$PtX_2(PMe_2Ph)_2$ (X = Cl, Br),[18] *trans*-$PtI_2(PMe_2Ph)_2$,[3] *cis*-$PtCl_2(PEt_3)_2$[19] (*trans*-$PtCl_2(PEt_3)_2$ used as starting material), *cis*- and *trans*-$PtBr_2(PEt_3)_2$,[7] *trans*-$PtI_2(PEt_3)_2$,[7] *cis*-$PtI_2(PEt_3)_2$ (methanol used as solvent and complex precipitated by addition of water), $PtClL_3^+$ (L = PMe_2Ph, PEt_3),[20] $PtXL_3^+$ (X = Br, I; L = PMe_2Ph, PEt_3) by metathetical replacement similar to the method described in ref 7, $Pt(PMe_2Ph)_4^{2+}$,[21] $PtX_2(PMe_2Ph)_3$ (X = Br, I)[6c,8] (PF_6^- was found to be a better counterion than ClO_4^- for the cationic complexes).

Instruments. IR spectra were recorded on a Beckman IR 12 using Nujol mulls, NMR spectra were recorded on a Varian HA100 or a Varian A-60, and dipole moments were measured using a Pulfrich refractometer and a WTW dipolemeter. Kinetics and UV–vis spectra were recorded on either a Cary 14 or 15 spectrophotometer with thermostated cell compartments.

Materials. All chemicals used for kinetic experiments were of AR grade.

Results

Preparation and Reactions of Complexes. The end products for the reactions

$$cis\text{-}, trans\text{-}PtX_2L_2 \xrightarrow{L} trans\text{-}, cis\text{-}PtX_2L_2, PtXL_3^+, PtX_2L_3, PtL_4^{2+} \qquad (6)$$
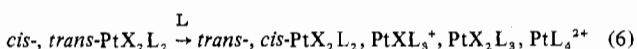
are listed in Table I. The times mentioned for the reactions are relative since the same amounts of catalytic, stoichiometric, and excess phosphine have been used in the reactions.

Dipole Moment Determination. In the initial preparation of $PtI_2(PEt_3)_2$ from *cis*- and *trans*-$PtCl_2(PEt_3)_2$ the same

$PtI_2(PEt_3)_2$ isomer was isolated. The dipole moment was therefore determined and the value of 0.52 D confirmed the *trans*-$PtI_2(PEt_3)_2$ isomer, since the cis species normally has a value of about 10 D.[22] The value of 0.52 D is most probably due to the presence of a small amount of cis species.

IR Spectra. *cis*- and *trans*-PtX_2L_2 isomers were identified by means of IR spectra. For the cis isomer, group theory predicts two IR-active platinum–phosphorus and platinum–halide vibrations and only one for the trans species.[9] The data are given in Table II.

NMR Spectra. The ^1H NMR spectra for *cis*- and *trans*-$PtX_2(PMe_2Ph)_2$ (X = Cl, Br, I) are well established.[7] The methyl resonances in (dimethylphenylphosphine)platinum(II) complexes occur as doublets (with ^{195}Pt satellites) when either one phosphine or two phosphines in a cis configuration are present. Two phosphines in a trans configuration give rise to a 1:2:1 triplet (with ^{195}Pt satellites) due to what is loosely known as virtual coupling.[10] When three phosphines are present in a square-planar complex, i.e., one cis and two trans phosphines, the ^1H NMR spectrum consists of a 1:2 combination of the cis doublets and trans triplets. These spectra are given in Table III.

In the case of triethylphosphine the spectra are much more complicated. However with the present knowledge of $J(P-H)$, $J(P-P)$, and $J(Pt-H)$ values it was possible to extract values for these couplings, and they are given in Table IV. As can be seen from this table virtual coupling is still observed for both the methyl and methylene groups. However $^{195}Pt-H$ coupling was not found in the methyl-resonance pattern. These NMR spectra confirm the identification made by IR spectra for the cis and trans species.

UV–Vis Spectra and Reactions $PtX_2L_2 + L \rightarrow ...$ (Eq 6). The UV–vis spectra of *cis*- and *trans*-PtX_2L_2, $PtXL_3^+$, PtX_2L_3 (X = Cl, Br, I; L = PMe_2Ph, PEt_3), and $Pt(PMe_2Ph)_4^{2+}$ are given in Table V. These spectra were used in the identification of the end products in solution for the reactions *cis*- and *trans*-$PtX_2L_2 + L$ in methanol and pentane–10% dichloromethane (Table I). The concentration of L varied from zero to an approximately 30-fold excess.

The Five-Coordinate Complexes PtX_2L_3. Only $PtBr_2(PMe_2Ph)_3$ and $PtI_2(PMe_2Ph)_3$ could be isolated.[6c] Unfortunately crystals suitable for x-ray analysis were not formed but suitable crystals were obtained for the palladium analogues and $PdCl_2(PMe_2Ph)_3$ was subjected to crystallographic investigation. Figure 1 shows the ligand spatial orientation as well as the relevant bond lengths. The structure was found to be intermediate between trigonal bipyramidal and square pyramidal. A detailed molecular and crystal structure which includes an elaborate discussion on the one long Pd–Cl bond length (2.96 Å) has been published.[8] On the basis of the different $PdCl_2(PMe_2Ph)_3$ and $PdCl(PMe_2Ph)_3^+$ visible spectra the conclusion was drawn that this five-coordinate complex cannot be viewed as a tight ion pair.

For the cases (1) X = Cl; L = PMe_2Ph and (2) X = Cl, Br, I; L = PEt_3, different UV–vis spectra were obtained when excess L was added to PtX_2L_2. These spectra did not correspond to *cis*- or *trans*-PtX_2L_2, $PtXL_3^+$, or PtL_4^{2+}. PtX_2L_3, the only other likely species, was therefore most probably prepared in situ.

Kinetics of the Phosphine-Catalyzed Isomerization *cis*-PtI_2L_2 + L(+QI) → *trans*-PtI_2L_2 + L (Eq 4). Because of the air sensitivity of PMe_2Ph and PEt_3 all the reactions were initially done in both the presence and absence of oxygen. In no case was a difference in kinetic parameters observed and therefore air was not subsequently excluded.

From Table I it can be seen that PtX_2L_2 forms $PtXL_3^+$ or PtL_4^{2+} in methanol and PtX_2L_3 in pentane–10% dichloromethane mixtures with a stoichiometric or an excess amount

Table I. End Products for the Reactions of cis- and trans-PtX_2L_2 + L[a]

X = Cl, L = PEt_3	X = Br, L = PEt_3	X = I, L = PEt_3	X = Cl, L = PMe_2Ph	X = Br, L = PMe_2Ph	X = I, L = PMe_2Ph	Amount of L added	Isomer and solvent
No isom	No isom	Isom to trans in few weeks	No isom	No isom	Cis-trans equil with ip at 340 nm in ~1 week	No L	Cis in MeOH
No isom	Isom to trans in 1 day	Isom to trans in 6 h	No isom	No isom	Cis-trans equil with ip at 340 nm in few hours	Cat L	
$PtClL_3^+$	$PtBrL_3^+$	$PtIL_3^+$	$PtClL_3^+$	$PtBrL_3^+$	$PtIL_3^+$	Stoich L	
$PtClL_3^+$	$PtBrL_3^+$	$PtIL_3^+$	PtL_4^{2+}	Possibly PtL_4^{2+}	Possibly PtL_4^{2+}	Exc L	
No isom	No isom	No isom	No isom	No isom	Cis-trans equil with ip at 340 nm	No L	Trans in MeOH
No isom	No isom	No isom	No isom	No isom	Cis-trans equil with ip at 340 nm	Cat L	
$PtClL_3^+$ formed with ip at 287, 257, 247 nm	$PtBrL_3^+$	$PtIL_3^+$	$PtClL_3^+$	$PtBrL_3^+$	$PtIL_3^+$	Stoich L	
$PtClL_3^+$	$PtBrL_3^+$	$PtIL_3^+$	PtL_4^{2+}	Possibly PtL_4^{2+}	Possibly PtL_4^{2+}	Exc L	
Isom to trans with ip at 317 and 231 nm	Isom to trans in 12 h	Isom to trans in 1.5 h with ip at 348 nm	No isom	Isom in few min to trans	Isom to trans with ip at 345 nm	No L	Cis in pentane-10% CH_2Cl_2
As below	Isom to trans	Isom to trans with ip at 348 nm	No isom	Isom to trans	Isom to trans with ip at 345 nm	Cat L	
As below	As below	As below	As below	$PtBr_2L_3$	PtI_2L_3	Stoich L	
UV-vis spectrum changes to unknown	UV-vis spectrum changes to unknown	UV-vis spectrum changes to unknown; peak at 280 nm; shoulder at 300 nm	UV-vis spectrum changes to unknown	$PtBr_2L_3$ peak at 400 nm	PtI_2L_3 peak at 460 nm	Exc L	
No reaction	No reaction	No reaction	No reaction	No reaction	Isom to cis-trans equil	No L	Trans in pentane-10% CH_2Cl_2
No reaction	No reaction	No reaction	Isom to cis	No reaction	Isom to cis-trans equil	Cat L	
As below	As below	As below	As below	$PtBr_2L_3$	PtI_2L_3	Stoich L	
UV-vis spectrum changes to unknown	UV-vis spectrum changes to unknown	UV-vis spectrum changes to unknown	UV-vis spectrum changes to unknown	$PtBr_2L_3$ peak at 400 nm	PtI_2L_3 peak at 460 nm	Exc L	

[a] No isom = no isomerization in 3–5 days; isom = isomerization; cat = catalytic amount of; equil = equilibrium; stoich = stoichiometric amount of; ip = isosbestic point; exc = excess amount of. When no time limit is given, isomerization is relatively fast.

Table II. Infrared Spectra (600–250 cm^{-1}) for Some Triethylphosphine– and Dimethylphenylphosphine–Platinum(II) Complexes (Nujol Mull)[a]

Complex	ν_{Pt-P}	ν_{Pt-X}
trans-PtCl$_2$(PEt$_3$)$_2$[9]	415 m	341 s
cis-PtCl$_2$(PEt$_3$)$_2$[9]	442 m, 427 m	303 s, 281 s
trans-PtBr$_2$(PEt$_3$)$_2$[9]	411 m	
cis-PtBr$_2$(PEt$_3$)$_2$[9]	441 m, 427 m	
trans-PtI$_2$(PEt$_3$)$_2$[9]	409 m	
cis-PtI$_2$(PEt$_3$)$_2$	440 m, 427 m	
trans-PtCl$_2$(PMe$_2$Ph)$_2$	422 m	341 s
cis-PtCl$_2$(PMe$_2$Ph)$_2$	458 s, 438 m	314 s, 294 s
trans-PtBr$_2$(PMe$_2$Ph)$_2$	425 m	
cis-PtBr$_2$(PMe$_2$Ph)$_2$	453 s, 436 s	
trans-PtI$_2$(PMe$_2$Ph)$_2$	425 s	
cis-PtI$_2$(PMe$_2$Ph)$_2$	456 s, 440 s	

[a] s = strong; m = medium.

Table III. NMR Data on Methyl Resonances for Some Platinum(II)–Dimethylphenylphosphine Complexes in CDCl$_3$

| Complex	τ	Multiplicity	J, Hz
cis-PtCl$_2$(PMe$_2$Ph)$_2$[7]	8.2	Three doublets	^2J(P–H) = 11 ^3J(Pt–H) = 35
trans-PtCl$_2$(PMe$_2$Ph)$_2$	8.3	Three triplets	^2J(P–H) = 8 ^3J(Pt–H) = 23
cis-PtBr$_2$(PMe$_2$Ph)$_2$[7]	8.13	Three doublets	^2J(P–H) = 11 ^3J(Pt–H) = 35.5
trans-PtBr$_2$(PMe$_2$Ph)$_2$[a]			
cis-PtI$_2$(PMe$_2$Ph)$_2$[7]	8.05	Three doublets	^2J(P–H) = 10.5 ^3J(Pt–H) = 37
trans-PtI$_2$(PMe$_2$Ph)$_2$[7]	7.8	Three triplets	^2J(P–H) = 8 ^3J(Pt–H) = 25
PtCl(PMe$_2$Ph)$_3$$^+PF_6$$^-$	8.1	Three triplets	^2J(P–H) = 8 ^3J(Pt–H) = 24
	8.57	Three doublets	^2J(P–H) = 11 ^3J(Pt–H) = 41
PtBr(PMe$_2$Ph)$_3$$^+PF_6$$^-$	8.03	Three triplets	^2J(P–H) = 8 ^3J(Pt–H) = 24
	8.62	Three doublets	^2J(P–H) = 11 ^3J(Pt–H) = 40
PtI(PMe$_2$Ph)$_3$$^+PF_6$$^-$	7.92	Three triplets	^2J(P–H) = 7.5 ^3J(Pt–H) = 25
	8.68	Three doublets	^2J(P–H) = 11 ^3J(Pt–H) = 40
PtBr$_2$(PMe$_2$Ph)$_3$[b]	7.84	Three triplets	^2J(P–H) = 8 ^3J(Pt–H) = 23
	8.57	Three doublets	^2J(P–H) = 11 ^3J(Pt–H) = 42
PtI$_2$(PMe$_2$Ph)$_3$[b]	7.62	Three triplets	^2J(P–H) = 7.5 ^3J(Pt–H) = 23
	8.64	Three doublets	^2J(P–H) = 11 ^3J(Pt–H) = 41
Pt(PMe$_2$Ph)$_4$$^{2+}$2PF$_6$$^-$	8.3	Three broad singlets	^3J(Pt–H) = 26

[a] Preparation yield too small for NMR data. [b] Temperature had to be lowered in order to freeze out spectrum.

of phosphine. It is therefore not possible to study the isomerization using an excess of phosphine in order to achieve pseudo-first-order conditions. However, since the isomerization is catalyzed, the phosphine concentration remains constant throughout the reaction and can hence be treated as a pseudo-first-order reaction.

The kinetics of the catalyzed isomerization reaction 4 (L = PMe$_2$Ph, PEt$_3$) was studied using a constant catalytic amount of phosphine and varying an added amount of iodide. For L = PMe$_2$Ph the reaction was monitored at 360 nm and for L = PEt$_3$ the optical density (OD) change at 333 nm was followed. The plot for log (OD$_t$ – OD$_\infty$) vs. time (∞ = infinite time) yielded very good straight lines, indicating a first-order or pseudo-first-order reaction.

For both L = PMe$_2$Ph and PEt$_3$ a limiting curve was found for the k_{obsd} vs. [I$^-$] plot in both methanol (Q = Na) and benzene (Q = (n-Bu)$_4$N) and is shown in Figure 2. The spontaneous isomerization is so much slower that it did not
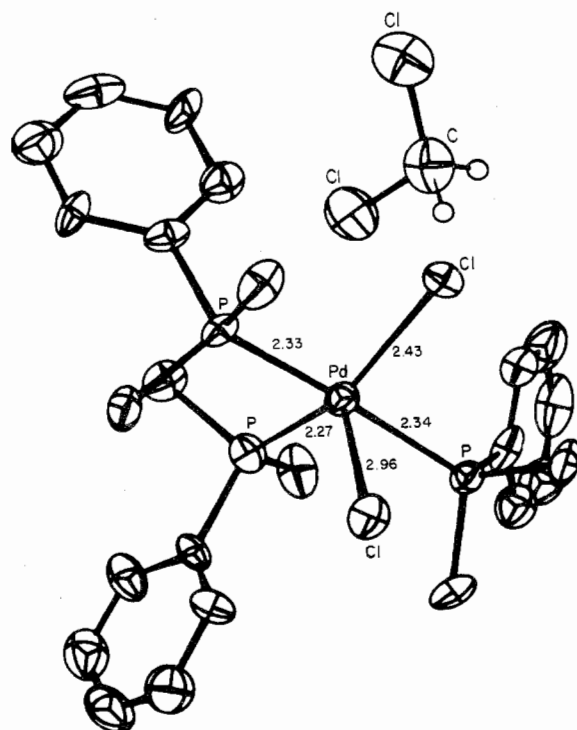
Figure 1. Molecular structure of PdCl$_2$(PMe$_2$Ph)$_3$.

show an intercept in the k_{obsd} vs. [I$^-$] plot.

$1/k_{obsd}$ vs. $1/[I^-]$ yielded a linear plot with an intercept (Figure 3). This type of behavior is typical of a fast associative–dissociative equilibrium followed by a rate-determining dissociative step,[11] e.g.

$$A + X \underset{}{\overset{K}{\rightleftharpoons}} C \overset{k}{\rightarrow} D + Y \qquad (7)$$

conforming to a rate law

$$k_{obsd} = \frac{kK[X]}{1 + K[X]} \qquad (8)$$

or

$$\frac{1}{k_{obsd}} = \frac{1}{k} + \frac{1}{kK[X]} \qquad (9)$$

Table VI lists the k_{obsd} values for these reactions for different [L], [Cl$^-$], temperature, and solvent.

It is evident that the k_{obsd} value, when no I$^-$ is added, is directly dependent on the phosphine concentration, as is the limiting value for high [I$^-$], whereas the slope of eq 9 is independent of the phosphine concentration (k or kK_2 in Table VII).

If the phosphine and iodide concentrations are introduced into eq 8 such that

$$k_{obsd} = \frac{kK[I^-][L]}{[I^-] + K[L]} \qquad (10)$$

or

$$\frac{1}{k_{obsd}} = \frac{1}{k[I^-]} + \frac{1}{kK[L]} \qquad (11)$$

empirical rate laws 10 and 11 can account for all of the data in Tables VII and VIII.

Since I$_2$ (and therefore I$_3$$^-$) can be formed photochemically from I$^-$ solutions, the possibility existed of I$_2$ or I$_3$$^-$ interfering in the reaction. This was prevented by preparing and keeping the I$^-$ solutions in the dark.

Table IV. NMR Data on Methyl and Methylene Resonances for some Platinum(II)–Triethylphosphine Complexes in CDCl$_3$

Complex	Methyl resonances			Methylene resonances		
	τ	Multiplicity	J, Hz	τ	Multiplicity	J, Hz
cis-PtCl$_2$(PEt$_3$)$_2$	8.8	1:2:2:2:1 quintet	^3J(H–H) = 7.5 ^3J(P–H) = 17.5 ^4J(Pt–H) = 0.0	7.88	1:4:6:4:1 quintet with ^{195}Pt satellites	^3J(H–H) = 7.5 ^2J(P–H) = 8.0 ^3J(Pt–H) = ~31^b
cis-PtBr$_2$(PEt$_3$)$_2$	8.8	1:2:2:2:1 quintet	^3J(H–H) = 7.5 ^3J(P–H) = 17.5 ^4J(Pt–H) = 0.0	7.8	1:4:6:4:1 quintet with ^{195}Pt satellites	^3J(H–H) = 7.5 ^2J(P–H) = 8.5 ^3J(Pt–H) = ~31^b
cis-PtI$_2$(PEt$_3$)$_2$	8.8	1:2:2:2:1 quintet	^3J(H–H) = 7.5 ^3J(P–H) = 17.5 ^4J(Pt–H) = 0.0	7.67	1:4:6:4:1 quintet with ^{195}Pt satellites	^3J(H–H) = 7.5 ^2J(P–H) = 7.5 ^3J(Pt–H) = ~44^b
trans-PtCl$_2$(PEt$_3$)$_2$	8.81	1:4:6:4:1 quintet	^3J(H–H) = 7.5 ^3J(P–H) = 16.0 ^4J(Pt–H) = 0.0		Multiplet	
trans-PtBr$_2$(PEt$_3$)$_2$	8.83	1:4:6:4:1 quintet	^3J(H–H) = 7.5 ^3J(P–H) = 17.0 ^4J(Pt–H) = 0.0		Multiplet	
trans-PtI$_2$(PEt$_3$)$_2$	8.88	1:4:6:4:1 quintet	^3J(H–H) = 7.5 ^3J(P–H) = 17.5 ^4J(Pt–H) = 0.0		Multiplet	
PtCl(PEt$_3$)$_3$$^+PF_6$$^-$	8.8	1:3.3:4.7:3.3:1 quintet^a	^3J(H–H) = 7.5 ^3J(P–H) = 18.0 ^4J(Pt–H) = 0.0		Multiplet	
PtBr(PEt$_3$)$_3$$^+PF_6$$^-$	8.8	1:3.3:4.7:3.3:1 quintet^a	^3J(H–H) = 7.5 ^3J(P–H) = 18.0 ^4J(Pt–H) = 0.0		Multiplet	
PtI(PEt$_3$)$_3$$^+PF_6$$^-$	8.78	1:3.3:4.7:3.3:1 quintet^a	^3J(H–H) = 7.5 ^3J(P–H) = 16.0 ^4J(Pt–H) = 0.0		Multiplet	

^{a} Appears to be a 2:1 mixture of the *trans*- and *cis*-PtX$_2$(PEt$_3$)$_2$ methyl patterns; J values given are the same for both the cis and trans phosphines in PtX(PEt$_3$)$_3$$^+$. ^{b} ^{195}Pt satellites obscured and values are therefore inaccurate.

Table V. UV–Vis Spectra for Some Platinum–Triethylphosphine and –Dimethylphenylphosphine Complexes^a

Complex	Methanol				Pentane–10% CH$_2$Cl$_2$			
Halide, phosphine	*cis*-PtX$_2$L$_2$	*trans*-PtX$_2$L$_2$	PtXL$_3$$^+$	PtL$_4$$^{2+}$	*cis*-PtX$_2$L$_2$	*trans*-PtX$_2$L$_2$	PtXL$_3$$^+$	PtX$_2$L$_3$
Cl, PEt$_3$	317, 262, 238	267, 248	242 sh		263 sh, 243	263, 249, 304 sh	243	
Br, PEt$_3$	292	280, 252 sh	240 sh		303, 252 sh	280, 250 sh	243 sh	
I, PEt$_3$	355, 280 sh, 250 sh, 233 sh	333, 300 sh, 284, 250 sh	324 sh, 280 sh, 240 sh, 220 sh		364, 283 sh, 257 sh	332, 303 sh, 287, 250 sh	328 sh, 280 sh	300 sh, 280
Cl, PMe$_2$Ph	310	268, 249	290 sh, 240 sh	240 sh	320 sh	264, 252	290 sh, 240 sh	350 sh
Br, PMe$_2$Ph	294 sh	278, 233 sh	265 sh, 240 sh		300 sh	280, 240	270 sh, 240 sh	373
I, PMe$_2$Ph	353	327, 287	325 sh, 240 sh		360	330, 310 sh, 292	325 sh, 245 sh	447

^{a} sh = shoulder.

The data given in Table VII for reaction 4 in benzene are clearly inconsistent and this is most probably due to incomplete dissociation of (*n*-Bu)$_4$NI.

Kinetics of the Iodide-Catalyzed Isomerization *cis*-PtI$_2$-(PEt$_3$)$_2$ + I$^-$ → *trans*-PtI$_2$(PEt$_3$)$_2$ + I$^-$ (Eq 5). *cis*-PtI$_2$(PEt$_3$)$_2$ isomerizes spontaneously in methanol within a few weeks at ambient temperatures. The addition of iodide ions however facilitates this isomerization in a few days. The kinetics of this reaction were studied.

Two reactions were observed with the spectral change of the first one corresponding to that of the cis to trans isomerization. No difference in kinetic parameters was found between dioxygen-containing and dioxygen-free solutions for the first reaction. The second reaction was also observed when I$^-$ was added to *trans*-PtI$_2$(PEt$_3$)$_2$.

The iodide solutions were prepared in the dark. No I$_3$$^-$ was detected in iodide solutions under the experimental conditions used to measure the kinetic results, i.e., with sporadic irradiation of the solution ($^1/_2$ min every 20 min) at 50 °C with 360-nm light for 2 days.

Because the second reaction was extremely slow it was impractical to follow the reactions to completion and then apply a curve-stripping technique to separate the two reactions represented by the log (OD$_t$ – OD$_\infty$) vs. time plot. Instead an OD$_\infty$ for the first reaction was estimated such that linear plots of log (OD$_t$ – OD$_\infty$) vs. time were obtained over 60% of

the reaction. These half-lives checked out with those obtained using the stripping technique.

Once again a limiting curve for the k_{obsd} vs. [I$^-$] plot without a noticeable intercept was observed due to the much slower spontaneous isomerization. A plot of $1/k_{obsd}$ vs. $1/[$I$^-]$ yielded a straight line. The empirical rate law

$$k_{obsd} = \frac{kK[\text{I}^-]}{1 + K[\text{I}^-]} \qquad (12)$$

can account for all the observed data given in Tables VIII and IX (k_{obsd} values, rate constants, and activation parameters).

Discussion

(1) The Reaction PtX$_2$L$_2$ + L → ... (Eq 6). It is of interest to note from Table I that in contrast to the generally accepted concept, except for PtCl$_2$(PMe$_2$Ph)$_2$, isomerization was found to proceed only from cis to trans in *both* methanol and pentane–10% dichloromethane. The previously published trans to cis isomerization for PtCl$_2$(PEt$_3$)$_2$ should read cis to trans.[12]

Isomerization in the platinum–halide–phosphine square-planar systems tends to proceed when a stable five-coordinate intermediate can be formed. This important conclusion can be drawn from Table I since it seems to be quite general that on addition of phosphine to *cis*- and *trans*-PtX$_2$L$_2$, PtXL$_3$$^+$ is formed in the polar solvent methanol, while PtX$_2$L$_3$ is formed in the nonpolar solvent pentane–10% dichloromethane.

Table VI. k_{obsd} Values for cis-PtI$_2$L$_2$ + L (+QI) → $trans$-PtI$_2$L$_2$ + L at 20 °C

[L], M	[I$^-$], M	k_{obsd}, s^{-1}
For L = PEt$_3$, Q = Na, Solvent = Methanol		
1.9 × 10^{-4}	0.2	0.144
	0.1	0.141
	0.075	0.128
	0.05	0.112
	0.04	0.099
	0.03	0.087
	0.02	0.075
	0.01	0.04
	0.005	0.027
	0.0	0.0018
1.2 × 10^{-4}	0.2	0.094
	0.1	0.087
	0.075	0.076
	0.05	0.06
	0.04	0.059
	0.03	0.039
	0.02	0.035
	0.01	0.025
	0.005	0.017
	0.0	0.001
For L = PEt$_3$, Q = (n = Bu)$_4$N, Solvent = Benzene		
2.16 × 10^{-5}	0.001	0.128
	0.00075	0.123
	0.0005	0.118
	0.00025	0.11
	0.0	0.096
1.95 × 10^{-4}	0.0	1.824
4.84 × 10^{-5}	0.0	0.239
2.42 × 10^{-5}	0.0	0.11
1.95 × 10^{-5}	0.0	0.095
0.95 × 10^{-5}	0.0	0.0247
1.95 × 10^{-6}	0.0	0.0056
For L = PMe$_2$Ph, Q = Na, Solvent = Methanol		
3.34 × 10^{-4}	0.2	0.86
	0.1	0.82
	0.075	0.77
	0.05	0.75
	0.04	0.64
	0.03	0.58
	0.02	0.46
	0.01	0.24
	0.005	0.14
	0.0	0.0224
3.9 × 10^{-4}	0.0	0.033
5.02 × 10^{-4}	0.0	0.038

Table VII. Rate and Equilibrium Constants for the Reaction

$$cis\text{-PtI}_2\text{L}_2 + \text{L} \xrightarrow{+QI} trans\text{-PtI}_2\text{L}_2 + \text{L}$$

[L], M	kK_e,^{a} kK_1,^{b} s^{-1} M^{-1}	k,^{a} kK_2,^{b} s^{-1} M^{-1}	$K_e{}^a$	Data source
For L = PEt$_3$, Q = Na, in Methanol at 20 °C				
1.9 × 10^{-4}	789	9.5	83	c
	880	6.3	50	d
1.2 × 10^{-4}	792	8.33	95	c
	595	4.35	136	d
	775		86	Limiting value^c vs. [L]
	825			Intercept^d vs. [L]
For L = PEt$_3$, Q = (n-Bu)$_4$N, in Benzene at 20 °C				
2.16 × 10^{-5}		4456		c
	2572	70	36.7	d
For L = PMe$_2$Ph, Q = Na, in Methanol at 20 °C				
3.35 × 10^{-4}	2689	66.9	40.2	c
	2988	45.6	65.5	d
3.91 × 10^{-4}		84.5		c
		75.0		d

^{a} Equation 15. ^{b} Equation 22. ^{c} Data from k_{obsd} vs. [I$^-$] plot. ^{d} Data from 1/k_{obsd} vs. 1/[I$^-$] plot.

Table VIII. k_{obsd} Values for the Reaction cis-PtI$_2$(PEt$_3$)$_2$ + I$^-$ → $trans$-PtI$_2$(PEt$_3$)$_2$ + I$^-$ (Eq 5) in Methanol

Temp, °C	[I$^-$], M	$10^5 k_{obsd}$, s^{-1}
35.1	1.0	6.75
	0.5	6.63
	0.25	4.94
	0.1	3.43
	0.05	2.53
40	1.0	8.05
	0.5	7.0
	0.25	5.83
	0.125	4.18
	0.1	4.5
	0.0625	3.4
	0.05	2.9
50	1.0	12.6
	0.5	11.7
	0.25	10.1
	0.2	8.9
	0.1	6.8
	0.05	5.0

Table IX. Rate and Equilibrium Constants for the Reaction cis-PtI$_2$(PEt$_3$)$_2$ + I$^-$ → $trans$-PtI$_2$(PEt$_3$)$_2$ + I$^-$ (Eq 5) in Methanol^a

Temp, °C	$10^5 k$,^{b} s^{-1}	K_e,^{b} M^{-1}	Data source
35.1	7.3		c
	7.57	9.2	d
40	8.5		c
	8.6	9.6	d
50	13.5		c
	14.7	8.3	d

^{a} $\Delta H^{\ddagger}$ = 8.3 ± 1.2 kcal mol^{-1}. ^{b} Equation 28. ^{c} Data from k_{obsd} vs. [I$^-$] plot. ^{d} Data from 1/k_{obsd} vs. 1/[I$^-$] plot.

However, catalyzed isomerization in methanol basically only follows for X = I, and then only at a very slow rate, whereas in pentane–10% dichloromethane, isomerization is very fast and proceeds in every single system studied.

A second important conclusion that can be drawn from Table I is that in the cases *where no catalyzed isomerization occurs, a Pt–P bond in PtXL$_3$$^+$ cannot be broken by an X$^-$ to form either cis- or trans-PtX$_2$L$_2$.* The validity of this statement is realized when one closely examines the consecutive displacement mechanism—eq 1. We know that the first step in this mechanism, the formation of PtXL$_3$$^+$, does occur even if no catalyzed isomerization is observed. Therefore the factor preventing isomerization must be the inability of a halide ion to break a Pt–P bond in PtXL$_3$$^+$.

In some cases (X = Cl, L = PEt$_3$, PMe$_2$Ph; X = Br, L = PMe$_2$Ph) no catalyzed isomerization was found in methanol, but isomerization proceeded in pentane–10% dichloromethane. In terms of the consecutive displacement mechanism this means that a Pt–P bond in PtXL$_3$$^+$ cannot be broken in methanol but can be broken in pentane–10% dichloromethane. It thus seems much more reasonable to invoke the pseudorotation mechanism involving a five-coordinate intermediate that is stabilized in nonpolar solvents to explain these results.

In going from X = Cl or Br to X = I, catalyzed isomerization proceeds very slowly in methanol. Two explanations for this involving either the consecutive displacement or the pseudorotation mechanisms are possible: (a) the iodide ion being a better nucleophile than Br$^-$ or Cl$^-$ may now be able to break a Pt–P bond or (b) in this iodide system it is perhaps possible to stabilize a five-coordinate intermediate in very small quantities in methanol, allowing only a very slow isomerization to take place.

The isomerization reaction is speeded up by orders of magnitude in changing from methanol to pentane–10% dichloromethane mixtures. The consecutive displacement mechanism can explain this by considering two opposing
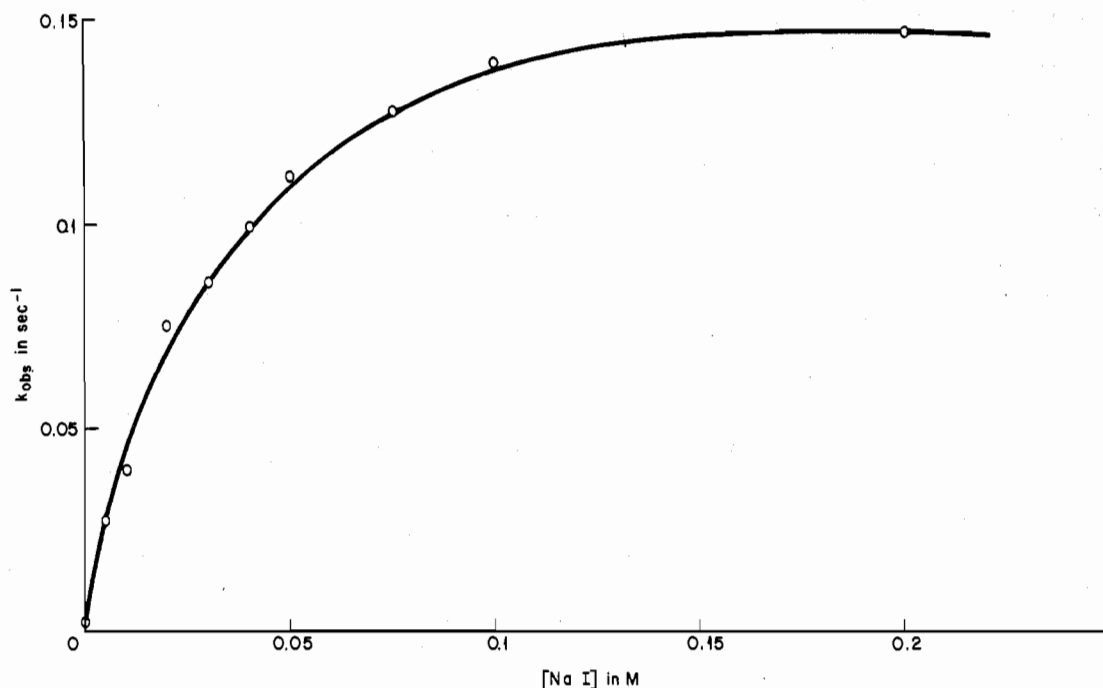
Figure 2. k_{obsd} vs. [NaI] for the reaction

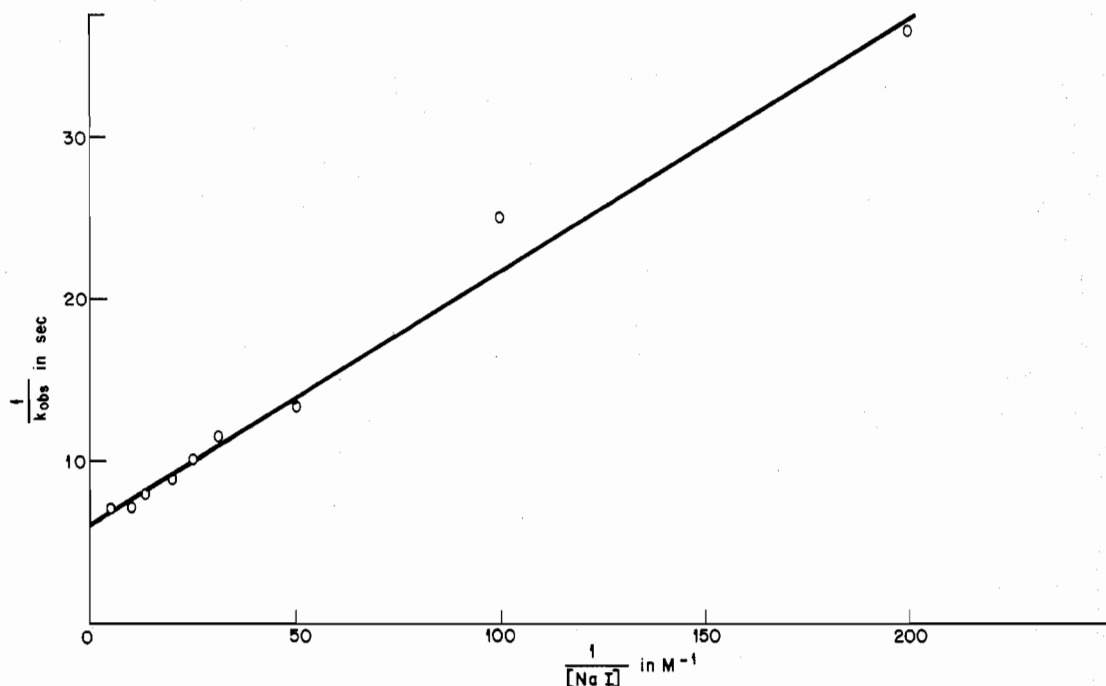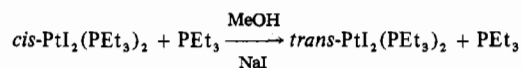$$cis\text{-PtI}_2(\text{PEt}_3)_2 + \text{PEt}_3 \xrightarrow[\text{NaI}]{\text{MeOH}} trans\text{-PtI}_2(\text{PEt}_3)_2 + \text{PEt}_3$$

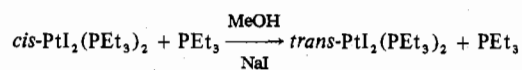**Figure 3.** $1/k_{obsd}$ vs. $1/[\text{NaI}]$ for the reaction

$$cis\text{-PtI}_2(\text{PEt}_3)_2 + \text{PEt}_3 \xrightarrow[\text{NaI}]{\text{MeOH}} trans\text{-PtI}_2(\text{PEt}_3)_2 + \text{PEt}_3$$

factors. First, the concentration of the relevant intermediate PtXL_3^+ is decreased by a few orders of magnitude and will therefore slow down the isomerization tremendously. Second, a halide becomes a much better nucleophile in a nonpolar solvent and the rate can increase by a few orders of magnitude.[23] This second factor would have to be the overriding one to explain these rate variations. For pseudorotation, the easier it is to stabilize the five-coordinate intermediate (i.e., in going from polar to nonpolar solvent and from Cl⁻ to Br⁻

to I⁻) the faster the isomerization will be.

(2) NMR Studies on the PtX₂L₂ + L Reaction. In his ¹H NMR study on the methyl resonance pattern of PtCl-$(\text{PMe}_2\text{Ph})_3^+$ in CDCl₃, Powell[3] interpreted the loss of the ^{195}Pt satellites and resolution on addition of Cl⁻ to the solution as being due to the breaking of a Pt–P bond caused by a mutual exchange of Cl⁻ and PMe₂Ph. He also found: "when PMe₂Ph is added to CDCl₃ solutions of cis-PtCl₂(PMe₂Ph)₂ at added PMe₂Ph to complex ratios of 0.5:1, the low-temperature n.m.r.
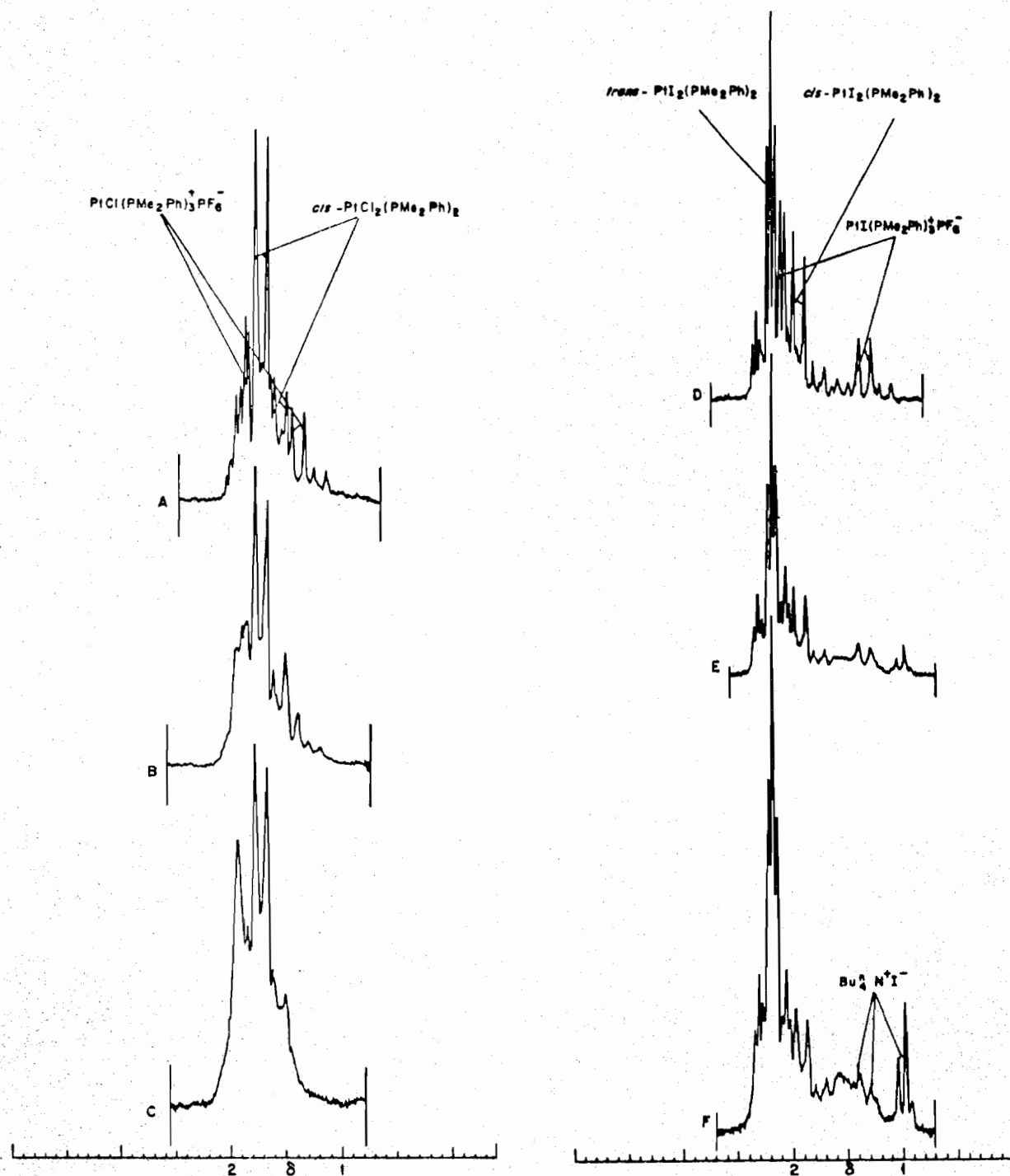
Figure 4. ^{1}H NMR for a mixture of *cis*-PtCl$_2$(PMe$_2$Ph)$_2$ and PtCl(PMe$_2$Ph)$_3$$^+PF_6$$^-$ in CDCl$_3$ (A), with a small amount of AsPh$_4$$^+Cl^-$ added (B), and for the CDCl$_3$ solution saturated with AsPh$_4$$^+Cl^-$ (C). ^{1}H NMR of a mixture of *cis*- and *trans*-PtI$_2$(PMe$_2$Ph)$_2$ and PtI(PMe$_2$Ph)$_3$$^+PF_6$$^-$ (D) and upon addition of successive amounts of (*n*-Bu)$_4$N$^+$I$^-$ (E, F).

shows the presence of ca. equal amounts of cis complex and chloride salt in the solution and no free PMe$_2$Ph. On warming to 20° the methyl proton resonances of both complex and salt coalesce into a single-resonance pattern and ^{195}Pt coupling is lost. This observation is consistent with the L-exchange mechanism involving consecutive L → Cl (trans to L) and Cl$^-$ → L (trans to L) SN2 substitutions." Further: "The n.m.r. spectrum of equal amounts of *cis*-PtCl$_2$(PMe$_2$Ph)$_2$ and PtCl(PMe$_2$Ph)$_3$$^+PF_6$$^-$ in CDCl$_3$ at 35° shows no sign of collapse of the individual methyl proton resonances owing to the lack of a free ligand capable of substituting a coordinated PMe$_2$Ph. Addition of [AsPh$_4$]$^+$Cl$^-$ to the solution collapses the methyl proton resonances." These experiments have been

repeated and only the collapse of the PtCl (PMe$_2$Ph)$_3$$^+$ methyl resonance has been found, as is shown in Figure 4, regardless of whether [AsPh$_4$]$^+$Cl$^-$ is added to a mixture of *cis*-PtCl$_2$-(PMe$_2$Ph)$_2$ and PtCl(PMe$_2$Ph)$_3$$^+PF_6$$^-$ or whether PMe$_2$Ph is added to *cis*-PtCl$_2$(PMe$_2$Ph)$_2$. Since this work has been done in nonpolar media, a five-coordinated species most probably exists (Table I) and the results must be viewed in the light of reaction scheme 13.

The collapse of the PtCl(PMe$_2$Ph)$_3$$^+$ methyl resonance while that of the *cis*-PtCl$_2$(PMe$_2$Ph)$_2$ is still resolved shows that no one-step Cl$^-$–PMe$_2$Ph mutual exchange is occurring. This collapse also cannot be explained by only pseudorotation between PtCl$_2$(PMe$_2$Ph)$_3$(A) and PtCl$_2$(PMe$_2$Ph)$_3$(B) (see

$$\text{(13)}$$
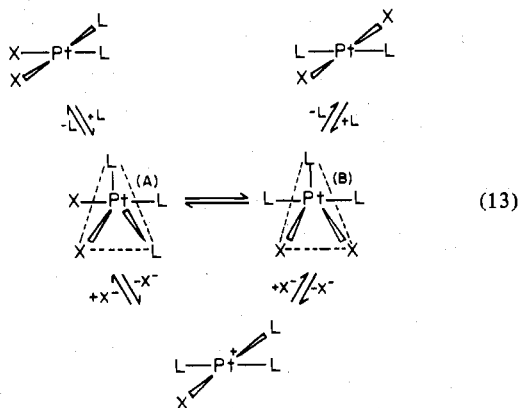
reaction scheme 13) since only a small percentage of Cl⁻ was added; therefore some resolved $PtCl(PMe_2Ph)_3{}^+$ methyl resonance will have to remain. This leaves the equilibrium between $PtCl_2(PMe_2Ph)_3(A)$ and $PtCl(PMe_2Ph)_3{}^+ + Cl^-$ to explain the phenomena, while it is impossible to say whether pseudorotation is proceeding simultaneously. The fact that the loss of the ^{195}Pt satellites is not due to the breaking of a Pt–P bond, as was concluded by Powell,[3] once again underlines the cautiousness with which conclusions from NMR–temperature studies must be made. However, since we know that $PtCl(PMe_2Ph)_3{}^+$ is formed from both *cis-* and *trans-*$PtCl_2$-$(PMe_2Ph)_2$ and a trans to cis catalyzed isomerization does occur, a slow Cl⁻–PMe$_2$Ph mutual exchange, at least between *cis-*$PtCl_2(PMe_2Ph)_2$ and $PtCl(PMe_2Ph)_3{}^+$, must be taking place.

Powell[3] also did some NMR studies on the iodide system. In this case PMe$_2$Ph was added to an equilibrium mixture of *cis-* and *trans-*$PtI_2(PMe_2Ph)_2$ in CDCl$_3$ at 0 °C, where formation of $PtI(PMe_2Ph)_3{}^+$ was evident. He further noted: "On warming this solution, collapse and coalescence of salt and *cis-*isomer methyl resonance with concurrent loss of ^{195}Pt coupling ($J_{^{195}Pt-H} = 35.8$ Hz) for *cis* isomer occurs prior to collapse and loss of ^{195}Pt coupling for the *trans-*isomer resonances ($J_{^{195}Pt-H} = 25.4$ Hz). This indicates that PMe$_2$Ph ligand exchange between *cis-*$PtI_2(PMe_2Ph)_2$ and PtI-$(PMe_2Ph)_3{}^+I^-$ is occurring faster than ligand exchange in *trans-*$PtI_2(PMe_2Ph)_2$ and faster than *cis–trans* isomerization." This NMR study has been repeated and the same behavior was found. However, when $(n\text{-Bu})_4N^+I^-$ was added to a mixture of $PtI(PMe_2Ph)_3{}^+PF_6{}^-$ and *cis-* and *trans-*PtI_2-$(PMe_2Ph)_2$ in CDCl$_3$, only the $PtI(PMe_2Ph)_3{}^+$ methyl resonance pattern collapsed (Figure 4D–F). This is most probably because only a very small amount of free I⁻ is introduced into the solution and once again the mutual exchange between halide and phosphine is not a one-step process, but rather the equilibrium between $PtI(PMe_2Ph)_3{}^+I^-$ and $PtI_2(PMe_2Ph)_3(A)$ is much faster than the equilibrium between $PtI_2(PMe_2Ph)_3(A$ or B) and *cis-* or *trans-*$PtI_2(PMe_2Ph)_2$, respectively. The observation by Powell[3] that the collapse of the methyl resonance for the cis isomer occurs prior to that of the trans isomer for the iodide system when the solution is heated can thus be explained by the equilibrium between *cis-*$PtI_2(PMe_2Ph)_2$ and $PtI_2(PMe_2Ph)_3(A)$ being faster than the equilibrium between *trans-*$PtI_2(PMe_2Ph)_2$ and $PtI_2(PMe_2Ph)_3(B)$ (reaction scheme 13). As a consequence of the collapse of the $PtI(PMe_2Ph)_3{}^+$ methyl resonance pattern (and for that matter the PtI_2-$(PMe_2Ph)_3$ methyl resonance pattern) it is impossible to say whether pseudorotation of $PtI_2(PMe_2Ph)_3$ is occurring as well.

In order for isomerization to occur via the consecutive displacement mechanism, the halide–phosphine mutual exchange in *both* the equilibria *cis-*PtX_2L_2–$PtXL_3{}^+X^-$ and *trans-*PtX_2L_2–$PtXL_3{}^+X^-$ will have to be faster than pseudorotation of PtX_2L_3. Therefore, although English, Meakin,

and Jesson[31] have shown that ligand dissociation from $HML_4{}^+$ is rapid relative to the rate of intramolecular arrangement in $HML_4{}^+$ and although the equilibria *cis-*PtX_2L_2 + L–$PtX_2L_3(A)$–$PtXL_3{}^+X^-$ may be faster than pseudorotation of PtX_2L_3, the pseudorotation may still be faster than the equilibrium $PtX_2L_3(B)$–$PtXL_3{}^+X^-$ (reaction scheme 13) and therefore cause isomerization to rather proceed via pseudorotation.

(3) Kinetics and Mechanisms of the Phosphine-Catalyzed Isomerization *cis-*PtI_2L_2 + L (+I) → *trans-*PtI_2L_2 + L **(Eq 4).** **(a) From the Consecutive Displacement Mechanism Viewpoint.** If the consecutive displacement pathway is considered for the isomerizations dealt with in this study, one would then expect the scheme for reaction 4 (using a *catalytic* amount of phosphine) to be

$$cis\text{-}PtI_2L_2 + L \overset{K_e}{\rightleftharpoons} PtIL_3{}^+ + I^- \overset{k}{\to} trans\text{-}PtI_2L_2 + L \qquad (14)$$
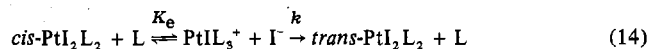
It has previously been suggested[3] that the intermediate for this reaction must be an ion pair $PtIL_3{}^+,I^-$. However, seeing that this reaction was carried out in methanol and it was found that $PtIL_3{}^+$ predominantly exists in this solvent, there is no basis for introducing the ion pair. The trans effect and nucleophilicity of ligands in square-planar substitution reactions are well established, and L is known to be a much better nucleophile than I⁻ and the replacement of a ligand trans to L to be much faster than that of the same ligand trans to I⁻. Therefore one would expect the preequilibrium in scheme 14 to be fast and the reaction described by k to be rate determining. The rate law for this scheme will then be

$$k_{obsd} = \frac{kK_e[L][I^-]}{[I^-] + K_e[L]} \qquad (15)$$

or

$$1/k_{obsd} = 1/kK_e[L] + 1/k[I^-] \qquad (16)$$

These rate laws are the same as the empirical rate laws 10 and 11 and can therefore account for all of the observed data. For example, at high [I⁻] the rate law will simplify to
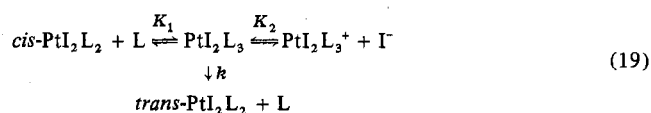
$$k_{obsd} = kK_e[L] \qquad (17)$$

thus explaining the direct dependence on [L] of the limiting k_{obsd} values. With no iodide added, $[I^-] \simeq [L]_0$ (where $[L]_0$ = added amount of L), since the equilibrium constant K_e is big and eq 15 becomes

$$k_{obsd} \simeq k[L]_0 \qquad (18)$$

This direct dependence on $[L]_0$ at $[I^-]_0$ was observed ($[I]_0 = [I^-]$ with no added I⁻ since free I⁻ is generated when phosphine is added).

(b) From the Pseudorotation Mechanism Viewpoint. If pseudorotation occurs, then the expected reaction scheme will be

$$cis\text{-}PtI_2L_2 + L \overset{K_1}{\rightleftharpoons} PtI_2L_3 \overset{K_2}{\rightleftharpoons} PtI_2L_3{}^+ + I^-$$
$$\downarrow k \qquad\qquad\qquad (19)$$
$$trans\text{-}PtI_2L_2 + L$$

It was found in the establishing of Table I that the equilibria described by K_1 and K_2 are very fast and the rate-determining step must be the dissociation to *trans-*PtI_2L_2 + L or the pseudorotation itself. The rate law for scheme 19 is

$$k_{obsd} = \frac{kK_1K_2[L][I^-]}{K_2[I^-] + K_1[L] + K_1K_2[L][I^-]} \qquad (20)$$

or

$$k_{obsd} = \frac{k}{\dfrac{1}{K_1[L]} + \dfrac{1}{K_2[I^-]} + 1} \qquad (21)$$

or

$$\frac{1}{k_{obsd}} = \frac{1}{kK_1[L]} + \frac{1}{kK_2[I^-]} + \frac{1}{k} \qquad (22)$$

In order for the reaction in scheme 19 to lie over to the right-hand side, K_2 must be small, and smaller than K_1. At very high $[I^-]$ rate law 20 simplifies to
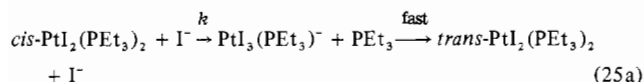
$$k_{obsd} = kK_1[L] \qquad (23)$$

and with no added iodide ($[I^-] \simeq [L]_0$) rate law 20 may simplify to

$$k_{obsd} \simeq kK_2[L]_0 \qquad (24)$$

The values found for $1/kK_1[L] + 1/k$ from eq 22 and $1/kK_1[L]$ from eq 23 compare very well, suggesting that $1/k$ is too small to contribute to the $1/kK_1[L]$ term.

The pseudorotation mechanism thus yields the same rate law as the consecutive displacement mechanism and it is therefore impossible to distinguish between the two mechanisms.

(4) Kinetics and Mechanisms of the Iodide-Catalyzed Isomerization *cis*-PtI$_2$(PEt$_3$)$_2$ + I$^-$ → *trans*-PtI$_2$(PEt$_3$)$_2$ + I$^-$ **(Eq 5). (a) From the Consecutive Displacement Mechanism Viewpoint.** Assuming this mechanism to be in operation, reaction scheme 25a can be visualized for reaction 5, taking
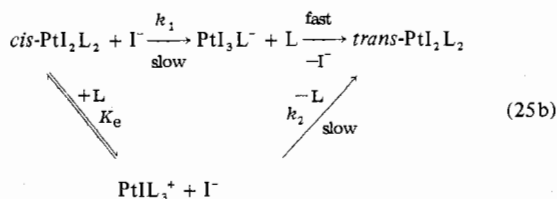
$$cis\text{-PtI}_2(\text{PEt}_3)_2 + \text{I}^- \xrightarrow{k} \text{PtI}_3(\text{PEt}_3)^- + \text{PEt}_3 \xrightarrow{\text{fast}} trans\text{-PtI}_2(\text{PEt}_3)_2 + \text{I}^- \qquad (25a)$$

into account the much bigger trans effect and nucleophilicity of PEt$_3$ compared to those for I$^-$. The rate law for this scheme will thus be the simple square-planar substitution rate law

$$k_{obsd} = k[I^-] \qquad (26a)$$

which does not resemble the empirical rate law 12. Thus the consecutive displacement mechanism cannot account for these experimental data.

The curvature in the k_{obsd} vs. $[I^-]$ plot found for reaction 5 cannot be explained by weak dissociation of NaI in methanol since the equivalent conductivity vs. $[\text{NaI}]^{1/2}$ plot (Figure 5) shows NaI to be extensively dissociated. Furthermore a plot of k_{obsd} vs. $[\text{NaI}]^{1/2}$ is still curved.

One referee pointed out that during reaction 25a PEt$_3$ is becoming free and therefore it is possible that this phosphine may catalyze the isomerization. The more elaborate reaction scheme 25b thus also demands consideration.

$$cis\text{-PtI}_2\text{L}_2 + \text{I}^- \underset{\text{slow}}{\xrightarrow{k_1}} \text{PtI}_3\text{L}^- + \text{L} \xrightarrow[-\text{I}^-]{\text{fast}} trans\text{-PtI}_2\text{L}_2$$

$$\searrow{}^{+\text{L}}_{K_e} \qquad\qquad {}^{-\text{L}}_{k_2}\nearrow_{\text{slow}} \qquad (25b)$$

$$\text{PtIL}_3{}^+ + \text{I}^-$$

The rate law for this reaction scheme does not conform with the empirical one

$$k_{obsd} = \frac{k_1[I^-]^2}{[I^-] + K_e[L]} + \frac{k_2K_e[I^-][L]}{[I^-] + K_e[L]} \qquad (26b)$$

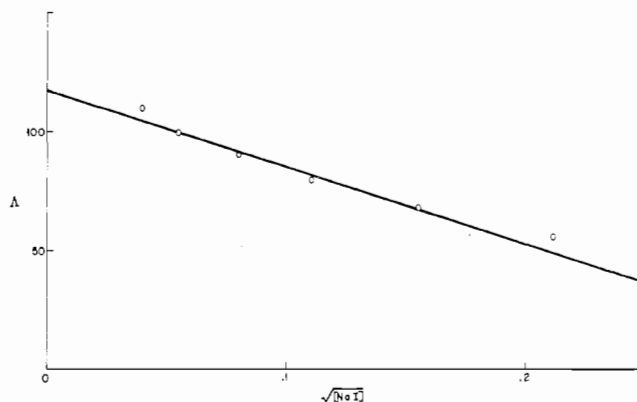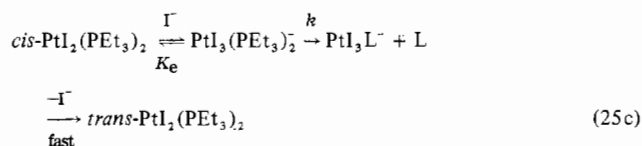but if it is assumed that the first term is negligibly small, this

Figure 5. Equivalent conductance of NaI in MeOH at 20 °C.

rate law can also explain the limiting dependence on $[I^-]$ of the empirical rate law 12 since
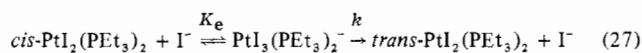
$$\frac{1}{k_{obsd}} = \frac{1}{k_2K_e[L]} + \frac{1}{k_2[I^-]} \qquad (26c)$$

However this k_2 value, which is of the order of 10^{-5} s^{-1} M^{-1} (Table IX), should now check out with the k value from reaction 14 which is of the order of 10 s^{-1} M^{-1} (Table VII). It is thus clear that a phosphine is most probably not exposed during reaction 25. The referee further proposed that a buildup of a five-coordinate intermediate can also explain the limiting dependence on $[I^-]$:

$$cis\text{-PtI}_2(\text{PEt}_3)_2 \underset{K_e}{\overset{\text{I}^-}{\rightleftharpoons}} \text{PtI}_3(\text{PEt}_3)_2^- \xrightarrow{k} \text{PtI}_3\text{L}^- + \text{L}$$

$$\xrightarrow[\text{fast}]{-\text{I}^-} trans\text{-PtI}_2(\text{PEt}_3)_2 \qquad (25c)$$

This has however no precedent in square-planar substitution reactions and it is therefore extremely doubtful whether this iodide-catalyzed system will exhibit this behavior.

(b) From the Pseudorotation Mechanism Viewpoint. Reaction scheme 27 shows how isomerization can be achieved

$$cis\text{-PtI}_2(\text{PEt}_3)_2 + \text{I}^- \overset{K_e}{\rightleftharpoons} \text{PtI}_3(\text{PEt}_3)_2^- \xrightarrow{k} trans\text{-PtI}_2(\text{PEt}_3)_2 + \text{I}^- \qquad (27)$$

by pseudorotation and the rate law for this scheme will be eq 28. This fits extremely well with the empirical rate law 12

$$k_{obsd} = \frac{kK_e[I^-]}{1 + K_e[I^-]} \qquad (28)$$

and a pseudorotation mechanism thus appears to be in operation for reaction 5. Though the intermediate PtI$_3$(PEt$_3$)$_2^-$ appears unusual, the palladium anion PdI$_3$(PMe$_2$Ph)$_2^-$ has been proposed as being formed in situ[13] from reactions of PdI$_2$(PMe$_2$Ph)$_2$ with I$^-$.

(5) Spontaneous Isomerization. As can be seen in Table I, spontaneous isomerization follows for all of the cases where X = I. This was also found to happen even faster in neat pentane solvent. Because pentane has no coordinating ability, this rules out the consecutive displacement mechanism involving pentane as a nucleophile. Pseudorotation of a five-coordinate halo-bridged dimer is still possible, and this is not unusual since the crystal structure of the red isomer of *trans*-PdI$_2$(PMe$_2$Ph)$_2$ shows that this complex exists as a polymer linked by iodide bridges.[14]

(6) Consecutive Displacement vs. Pseudorotation. For the sake of clarity it may be pertinent to summarize the observations presented thus far: (a) When, with addition of a catalytic amount of L to MX$_2$L$_2$, a five-coordinate intermediate can be stabilized (in nonpolar solutions), a very fast

isomerization results, but when MXL_3^+ is stabilized (in polar solvents), either no isomerization or an extremely slow isomerization occurs. (b) The empirical rate law derived from the kinetic data found for reaction 4 (the phosphine-catalyzed isomerization) can be explained by both the consecutive displacement and pseudorotation mechanisms. (c) The empirical rate law derived from the kinetic data found for reaction 5 (the iodide-catalyzed isomerization) can best be explained by the pseudorotation mechanism. (d) Spontaneous isomerization can best be explained by the pseudorotation mechanism.

A halide is about 4–6 orders of magnitude weaker as a nucleophile and trans group when compared to a phosphine and about the same orders of magnitude better as an outgoing ligand.[15] Considering that the rate constant for the reaction

$$trans\text{-}PtCl_2(PEt_3)_2 + {}^{36}Cl^- \xrightarrow{k} trans\text{-}PtCl^{36}Cl(PEt_3)_2 + Cl^- \quad (29)$$
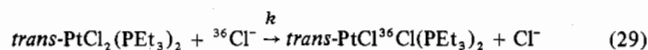
(a chloride replacing a chloride trans to a chloride) is 2.9×10^{-5} s^{-1} M^{-1} at 30 °C in methanol,[16] the rate of the second step in mechanism 1

$$PtCl(PEt_3)_3^+ + Cl^- \to trans\text{-}PtCl_2(PEt_3)_2 + L \quad (30)$$
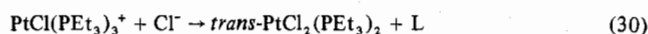
(a chloride replacing a phosphine trans to a chloride) can be expected to be almost immeasurably slow. (It was found that the charge on the complex and the cis group did not have an appreciable influence on the square-planar substitution rate.[15]) It is therefore not surprising for some of the chloride and bromide complexes in reaction 6 that no phosphine-catalyzed isomerization was observed in methanol after a few days, and it is most improbable that Cl$^-$ or Br$^-$ will become such good nucleophiles in pentane–10% dichloromethane as to facilitate isomerization in the order of minutes and seconds, respectively. Furthermore, if the kinetic evidence points to an iodide-catalyzed isomerization in methanol via the intermediate $PtI_3L_2^-$, then an isomerization through PtI_2L_3 for the phosphine-catalyzed reaction in methanol and benzene seems much more likely.

Although it thus seems possible for isomerization to proceed via a consecutive displacement mechanism, this process for the phosphine systems appears to be so slow in nonpolar as well as polar solvents that the pseudorotation mechanism is the faster and hence dominant pathway.

In changing from phosphines to ligands with nucleophilicities comparable to those of the halides (e.g., $PtCl_2(H_2O)_2$, $PtCl_2Br_2$, $PtCl_2(am)_2$) one would expect the consecutive displacement mechanism to be in operation, since five-coordination in such "hard" complexes is not likely. It is therefore not surprising that this mechanism has been proven kinetically for the $cis\text{-}PdCl_2(am)_2$ (ammine catalyzed) isomerization.[25]

Finally, the reason that the square-planar substitution reactions are stereospecific is the generation of a very specific five-coordinate transition state with such a short lifetime that pseudorotation is not possible, whereas in the case of the phosphine systems a five-coordinate intermediate is now stabilized. However, the substitution reactions of these phosphine systems are mostly done in polar solvents where the five-coordinate intermediate is not stabilized in appreciable amounts. Also, in order that nonstereospecific substitution occurs, pseudorotation will have to proceed faster than the substitution or at least at the same rate as substitution.

(7) Isomerization via a Three-Coordinate Intermediate. Kinetic studies of some uncatalyzed cis–trans isomerizations have recently been published[24] (scheme 31).

Since the rate at which bromide or chloride in $cis\text{-}PtXR$-$(PEt_3)_2$ is replaced by methanol or ethanol is much faster than k_i, it was concluded that this isomerization cannot occur via a consecutive displacement mechanism involving a solvent

$$cis\text{-}PtXR(PEt_3)_2 \xrightarrow[\substack{MeOH \\ EtOH}]{k_i} trans\text{-}PtXR(PEt_3)_2 \quad (31)$$
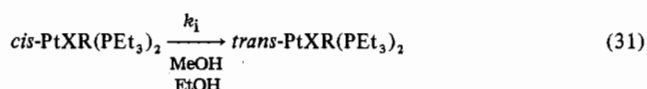
(X = Br, R = C_6H_5, $p\text{-}MeC_6H_4$, $o\text{-}MeC_6H_4$, $o\text{-}EtC_6H_4$, $2,4,6\text{-}Me_3C_6H_2$; X = Cl, R = o-tolyl, CH_3, C_2H_5, C_6H_5)
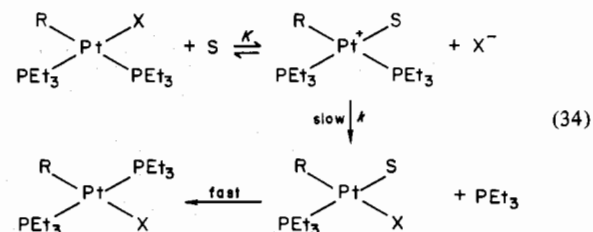
species. From the mass law retardation effect of halide ions on the isomerization rate, reaction scheme 32 was proposed,
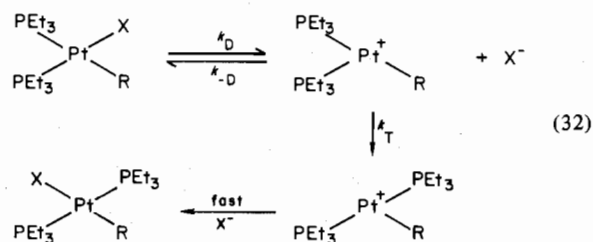
from which rate law 33 was derived.

$$k_i = \frac{k_D k_T}{k_{-D}[Cl^-] + k_T} \quad (33)$$

If however, one considers the full reaction scheme for this uncatalyzed isomerization reaction from the consecutive displacement viewpoint (eq 34) it is evident simply on the basis

of well-known incoming, trans, and outgoing ligand effects, that the first solvolysis reaction should not be the rate-determining step but rather that the substitution of PEt_3 by X$^-$ is. The difference between this substitution reaction and reaction 30 is that here the PEt_3 has an R group trans to it, which would cause the rate of this almost immeasurably slow step to increase by 4–6 orders of magnitude. This is still not enough to make this step faster than the solvolysis reaction but enough to make the consecutive displacement mechanism faster than the pseudorotation mechanism.

The rate law derived from reaction scheme 34

$$k_{obsd} = \frac{kK}{K + [Cl^-]} \quad (35)$$

has the same form as (33) and can therefore also explain all of the observed data.

Furthermore, mechanism 32 cannot explain the iodide-catalyzed isomerization of $cis\text{-}PtI_2(PEt_3)_2$ (reaction 5) since rate law 33 (predicting a mass law retardation effect by iodide ions) does not fit empirical rate law 12 which describes a direct limiting dependence on iodide ions.

The pseudorotation mechanism (involving a halide-bridged dimer) cannot explain these uncatalyzed isomerization reactions, eq 31, since the rate law derived from such a reaction scheme shows the observed reaction to be second order. There is also difficulty in explaining the mass law retardation effect of halide ions by this mechanism.

In substituting both halide groups in $PtX_2(PEt_3)_2$ by alkyl groups to form $PtR_2(PEt_3)_2$ (R = Me) no catalyzed or uncatalyzed isomerization was observed.[26] The consecutive displacement mechanism would be unusual in this case as it requires the formation of alkyl anions. The reason the pseudorotation mechanism is not in operation is most probably
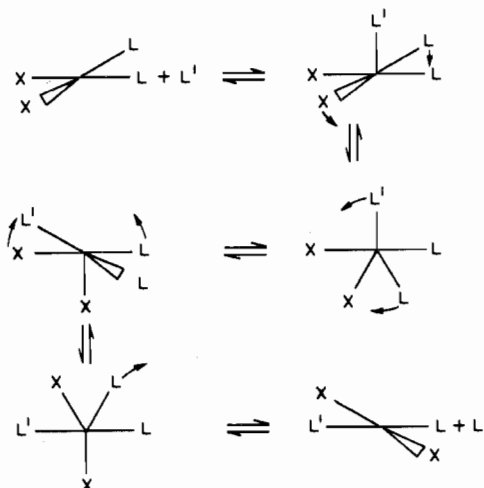
Figure 6. Isomerization by Berry pseudorotation.

that the complex is too "soft" to form a stable five-coordinate complex with a phosphine ligand since it is known that if too many "soft" ligands are coordinated around a "soft" metal ion the system becomes unstable.[27,30] Thus in changing to the "harder" Au^{3+} metal ion, cis–trans isomerization was observed for $AuMe_2R(PPh_3)$ (R = Et, *n*-Pr, *i*-Pr) with added phosphine.[28] However, because the rate of isomerization in this gold(III) system was *relatively* unaffected by added triphenylphosphine, it was concluded that the mechanism was an unimolecular process involving an equilibrium between square-planar and tetrahedral arrangements. However, this route is symmetry forbidden.[5] The observation that the rate of the *cis*- to *trans*-$AuMe_2Et(PPh_3)$ isomerization was *relatively* unaffected by the addition of successively more triphenylphosphine is hardly surprising as we see from rate law 20 in the pseudorotation mechanism discussion (which will now simplify to rate law 36 since K_2 in this $AuMe_2Et(PPh_3)$ case

$$k_{obsd} = \frac{kK_1[L]}{1 + K_1[L]} \tag{36}$$

will be very big) k_{obsd} has a limiting dependence on $[PPh_3]$ and the work was very probably done in the limiting region.

(8) Pseudorotation via Berry Pseudorotation. The geometry of the crystal structure of $PdCl_2(PMe_2Ph)_3$[8] lies between trigonal bipyramidal (TBP) and square pyramidal (SP). One would therefore expect Berry pseudorotation[17] to be a very likely mechanism whereby pseudorotation can occur, since this mechanism is basically an equilibrium between the TBP and SP geometries. Isomerization by this mechanism is shown in Figure 6 and shows that phosphine mixing can occur.

Conclusions

In conclusion pseudorotation appears to be the mechanistic pathway for spontaneous and iodide-catalyzed isomerization reactions for PtX_2L_2 systems (X = halide, L = phosphine) (and most probably also for arsine and stibine systems), whereas this mechanism is also favored for the phosphine-catalyzed isomerizations in both polar and nonpolar systems.

When one of the halide groups in PtX_2L_2 is replaced by a group with a much greater trans effect such as an alkyl or aryl group to form $PtXRL_2$, the consecutive displacement mechanism becomes the dominant pathway for the uncatalyzed isomerization in polar solvents and may also become the dominant path for phosphine-catalyzed isomerizations in both polar and nonpolar media.

In substituting two halide groups in PtX_2L_2 by alkyl or aryl groups to form PtR_2L_2, only the pseudorotation mechanism can explain isomerization, as is the case with $AuR_2R'L$ systems. For the amine–halo systems $MX_2(am)_2$ (M = Pt,

Pd) the consecutive displacement mechanism has previously been proved kinetically, and the aquo–halo systems most probably also follow this pathway.

Appendix. Derivation of Rate Laws

For

$$cis\text{-}PtI_2L_2 + L \underset{K_e}{\rightleftharpoons} PtIL_3^+ + I^- \overset{k}{\rightarrow} trans\text{-}PtI_2L_2 + L \tag{a}$$
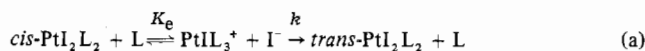
$$K_e = \frac{[PtIL_3^+][I^-]}{[cis\text{-}PtI_2L_2][L]}$$

Therefore

$$[cis\text{-}PtI_2L_2] = \frac{[PtIL_3^+][I^-]}{K_e[L]} \tag{i}$$

By substituting $[cis\text{-}PtI_2L_2]$ in the equation

$$[complex]_t = [cis\text{-}PtI_2L_2] + [PtIL_3^+]$$

$$= [PtIL_3^+]\left(\frac{[I^-]}{K_e[L]} + 1\right)$$

we have

$$[PtIL_3^+] = \frac{[complex]_t}{\dfrac{[I^-]}{K_e[L]} + 1} \tag{ii}$$
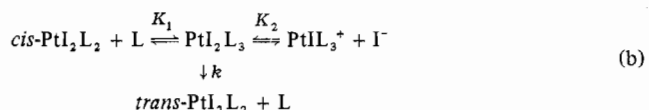
It is therefore possible to get the $[PtIL_3^+]$ in terms of the total complex concentration. The differential equation for the above reaction is

$$\frac{d[complex]_t}{dt} = k[PtIL_3^+][I^-] \tag{iii}$$

By substitution of the $[PtIL_3^+]$ in eq iii by eq ii followed by integration and introduction of $t_{1/2}$ ($k_{obsd} = 0.693/t_{1/2}$) the following rate law is obtained

$$k_{obsd} = \frac{kK_e[L][I^-]}{[I^-] + K_e[L]}$$

For

$$cis\text{-}PtI_2L_2 + L \underset{K_1}{\rightleftharpoons} PtI_2L_3 \underset{K_2}{\rightleftharpoons} PtIL_3^+ + I^- \tag{b}$$
$$\downarrow k$$
$$trans\text{-}PtI_2L_2 + L$$

$$K_1 = \frac{[PtI_2L_3]}{[cis\text{-}PtI_2L_2][L]}$$

and

$$K_2 = \frac{[PtI_2L_3]}{[PtIL_3^+][I^-]}$$

Therefore

$$[cis\text{-}PtI_2L_2] = \frac{[PtI_2L_3]}{K_1[L]} \tag{iv}$$

and

$$[PtIL_3^+] = \frac{[PtI_2L_3]}{K_2[I^-]} \tag{v}$$

The total complex concentration in solution to react is

$$[complex]_t = [cis\text{-}PtI_2L_2] + [PtI_2L_3] + [PtIL_3^+] \qquad (vi)$$

By substitution of $[cis\text{-}PtI_2L_2]$ and $[PtIL_3^+]$ in eq vi for eq iv and v it is possible to write the $[PtI_2L_3]$ in terms of $[complex]_t$

$$[PtI_2L_3] = \frac{[complex]_t}{\dfrac{1}{K_1[L]} + 1 + \dfrac{1}{K_2[I^-]}} \qquad (vii)$$
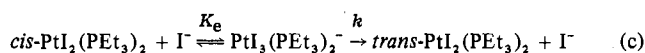
The differential equation for the above reaction is

$$\frac{d[complex]_t}{dt} = k[PtI_2L_3] \qquad (viii)$$

By introducing eq vii in eq viii and integrating, the following rate law is derived

$$k_{obsd} = \frac{kK_1K_2[L][I^-]}{K_2[I^-] + K_1K_2[I^-][L] + K_1[L]}$$

For

$$cis\text{-}PtI_2(PEt_3)_2 + I^- \underset{K_e}{\overset{}{\rightleftharpoons}} PtI_3(PEt_3)_2^- \overset{k}{\rightarrow} trans\text{-}PtI_2(PEt_3)_2 + I^- \qquad (c)$$

$$K_e = \frac{[PtI_3(PEt_3)_2^-]}{[cis\text{-}PtI_2(PEt_3)_2][I^-]}$$

Therefore

$$[cis\text{-}PtI_2(PEt_3)_2] = \frac{[PtI_3(PEt_3)_2^-]}{K_e[I^-]} \qquad (ix)$$

The total complex concentration to react is

$$[complex]_t = [cis\text{-}PtI_2(PEt_3)_2] + [PtI_3(PEt_3)_2^-] \qquad (x)$$

Substituting eq ix in eq x, we get
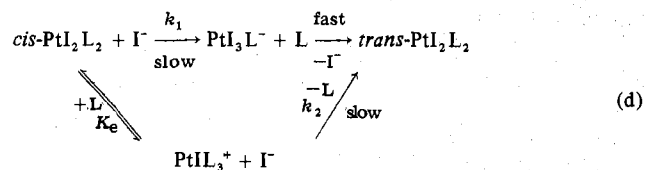
$$[PtI_3(PEt_3)_2^-] = \frac{[complex]_t}{\dfrac{1}{K_e[I^-]} + 1} \qquad (xi)$$

The differential equation for the above reaction is

$$\frac{d[complex]_t}{dt} = k[PtI_3(PEt_3)_2^-] \qquad (xii)$$

Substituting eq xi in eq xii and integrating, we get

$$k_{obsd} = \frac{kK_e[I^-]}{1 + K_e[I^-]}$$

For

$$cis\text{-}PtI_2L_2 + I^- \overset{k_1}{\underset{slow}{\longrightarrow}} PtI_3L^- + L \overset{fast}{\underset{-I^-}{\longrightarrow}} trans\text{-}PtI_2L_2 \qquad (d)$$

with branches $+L$, K_e (slow) and $-L$, k_2 (slow) leading to

$$PtIL_3^+ + I^-$$

$$K_e = \frac{[PtIL_3^+][I^-]}{[cis\text{-}PtI_2L_2][L]}$$

Therefore

$$[PtIL_3^+] = \frac{K_e[cis\text{-}PtI_2L_2][L]}{[I^-]} \qquad (xiii)$$

and

$$[cis\text{-}PtI_2L_2] = \frac{[PtIL_3^+][I^-]}{K_e[L]} \qquad (xiv)$$

The total complex concentration to react is

$$[complex]_t = [cis\text{-}PtI_2L_2] + [PtIL_3^+] \qquad (xv)$$

Substituting (xiii) and (xiv) in (xv), we get

$$[cis\text{-}PtI_2L_2] = \frac{[complex]_t}{\dfrac{K_e[L]}{[I^-]} + 1} \qquad (xvi)$$

or

$$[PtIL_3^+] = \frac{[complex]_t}{\dfrac{[I^-]}{K_e[L]} + 1} \qquad (xvii)$$

The differential equation for the above reaction is

$$\frac{d[complex]_t}{dt} = k_1[cis\text{-}PtI_2L_2][I^-] + k_2[PtIL_3^+][I^-] \qquad (xviii)$$

Substituting (xvi) and (xvii) in (xviii) and integrating, we get

$$k_{obsd} = \frac{k_1[I^-]^2}{[I^-] + K_e[L]} + \frac{k_2K_e[I^-][L]}{[I^-] + K_e[L]}$$

Registry No. $cis\text{-}PtCl_2(PEt_3)_2$, 15692-07-6; $cis\text{-}PtBr_2(PEt_3)_2$, 15636-78-9; $cis\text{-}PtI_2(PEt_3)_2$, 35084-99-2; $cis\text{-}PtCl_2(PMe_2Ph)_2$, 15393-14-3; $cis\text{-}PtBr_2(PMe_2Ph)_2$, 15616-81-6; $cis\text{-}PtI_2(PMe_2Ph)_2$, 41119-52-2; $trans\text{-}PtCl_2(PEt_3)_2$, 13965-02-1; $trans\text{-}PtBr_2(PEt_3)_2$, 13985-90-5; $trans\text{-}PtI_2(PEt_3)_2$, 15636-79-0; $trans\text{-}PtCl_2(PMe_2Ph)_2$, 38928-82-4; $trans\text{-}PtBr_2(PMe_2Ph)_2$, 29143-70-2; $trans\text{-}PtI_2(PMe_2Ph)_2$, 41119-53-3; $PtCl(PMe_2Ph)_3^+PF_6^-$, 27115-97-5; $PtBr(PMe_2Ph)_3^+PF_6^-$, 62207-73-2; $PtI(PMe_2Ph)_3^+PF_6^-$, 62207-75-4; $PtCl_2(PMe_2Ph)_3$, 62207-71-0; $PtBr_2(PMe_2Ph)_3$, 62989-37-1; $PtI_2(PMe_2Ph)_3$, 62989-36-0; $Pt(PMe_2Ph)_4^{2+}2PF_6^-$, 27115-98-6; $PtI_2(PEt_3)_3$, 62905-95-7; $PtCl(PEt_3)_3^+PF_6^-$, 62905-94-6; $PtBr(PEt_3)_3^+PF_6^-$, 62960-60-5; $PtI(PEt_3)_3^+PF_6^-$, 62905-93-5; K_2PtCl_4, 10025-99-7.

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Syntheses and Properties of the Ruthenium(III) Complexes *cis*- and *trans*-Ru(NH₃)₄(L)X²⁺. Application of Cyclic Voltammetry to Study Cis and Trans Effects on Substitution Reactions of the Ruthenium(II) Analogues

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Reported are the syntheses, spectral properties, and formal reduction potentials (E_f) of the mixed ligand complexes *cis*- and *trans*-Ru(NH₃)₄(L)X²⁺ (L = pyridine or isonicotinamide, X⁻ = Cl⁻, Br⁻, or I⁻; L = acetonitrile, X⁻ = Cl⁻). Each of the haloruthenium(III) complexes in aqueous solution displays a ligand to metal charge-transfer electronic spectral absorption band which is markedly dependent on the nature of X⁻ and modestly dependent on the nature of L. In contrast, whether X⁻ is Cl⁻, Br⁻, or I⁻ has little influence on E_f while L is much more influential following the order NH₃ < pyridine < isonicotinamide < acetonitrile. In addition cyclic voltammetry methods were used to examine the kinetics of halide aquation from the ruthenium(II) analogues Ru(NH₃)₄(L)X⁺. The rates for this reaction are relatively independent of the identity of X⁻ but are strongly dependent on the character and stereochemistry of L. π-Acceptor ligands such as pyridine slow the reaction in comparison to the pentaammine complex, an effect attributed to the increased effective charge on the Ru(II) site. The patterns of ruthenium(II) substitution labilities measured in this laboratory and others are summarized to give separate series for the cis effect and the trans effect of L in Ru(NH₃)₄(L)X⁺. The trans effect series is argued to be dominated by the σ-donor ability of the trans ligand with strong σ donors having a labilizing effect on the trans position. π-Acceptor ligands which are not strong σ donors deactivate both the cis and trans sites. For the more limited cis series the only L's known to be labilizing are of π donor character and this is rationalized in terms of the bonding factors in the transition state of a dissociative mechanism.

The chemistry of ruthenium(II) and ruthenium(III) ammine complexes has been an area of considerable activity in recent years.[3-7] A variety of observations have demonstrated that the Ru(II) and Ru(III) centers show contrasting characters with regard to π-symmetry interactions with coordinated ligands; i.e., Ru(II) is a good π donor[4] while the 4d⁵ Ru(III) is a good π acceptor.[8] The contrasting π-bonding properties lend particular interest to those complexes where both a π-donor and a π-acceptor ligand are in the same coordination sphere. The syntheses and properties of several such ruthenium(III) species, *cis*- and *trans*-Ru(NH₃)₄(L)X²⁺, are described here.

The reported data include the results of cyclic voltammetry (CV) studies on these mixed-ligand complexes. The CV experiment can provide formal reduction potentials for Ru(III)/Ru(II) complexes from the reversible waves of the cyclic scan[3,9] and kinetics information for reactions of the analogous ruthenium(II) complexes produced at the electrode, if the reaction rates fall within the time scale of the cyclic scan.[3,10] The reaction of interest in this context is the loss of halide ion (X⁻) from the Ru(II) coordination sphere (eq 1). Although

$$\text{Ru(NH}_3)_4(\text{L)X}^+ + \text{H}_2\text{O} \xrightarrow{k_1} \text{Ru(NH}_3)_4(\text{L)H}_2\text{O}^{2+} + \text{X}^- \tag{1}$$
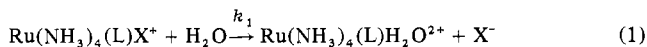
the halide is relatively substitution inert in the coordination sphere of Ru(III), it is quite labile in the Ru(II) sphere. This has been demonstrated by Kuempel and co-workers[10a] who used the CV technique to examine the aquation kinetics for Ru(NH₃)₅Cl⁺ and Ru(NH₃)₅Br⁺. The present studies have particular interest in the context of several investigations[6,7a]

of rate effects induced by variations of the ligand L for the substitution reactions of Ru(NH₃)₄(L)H₂O²⁺ (eq 2).

$$\text{Ru(NH}_3)_4(\text{L)H}_2\text{O}^{2+} + \text{N} \xrightarrow{k_2} \text{Ru(NH}_3)_4(\text{L)(N)}^{2+} + \text{H}_2\text{O} \tag{2}$$
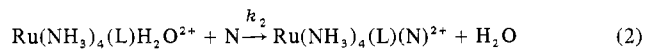
Analogous reactions for the pentaammine complex Ru(NH₃)₅H₂O²⁺ have been argued to proceed via a dissociative mechanism.[11,12] Thus, the question is raised whether the effects by various L predominantly reflect perturbations on the rates of H₂O dissociation or on the competition between solvent H₂O and the incoming nucleophile N for the coordinatively unsaturated intermediate. Insight into this question is provided by the CV technique which allows a more direct observation of the loss of X⁻ from the Ru(II).

Experimental Section

Materials. [*cis*-Ru(NH₃)₄Cl₂]Cl, [*trans*-Ru(NH₃)₄(SO₂)Cl]Cl, and [*trans*-Ru(NH₃)₄Cl₂]Cl were prepared by the literature procedures.[13] Ligands used in syntheses were reagent grade and were used without further purification. Potassium *p*-toluenesulfonate (KpTS) employed in electrochemical measurements was prepared as described.[3] Redistilled water was used in all solution preparation.

Analysis. Carbon/hydrogen/nitrogen microanalyses were performed by Galbraith Laboratories of Knoxville, Tenn. Ruthenium analyses were carried out using Malouf's modification of several earlier procedures.[14] In a typical determination, 8 mg of the ruthenium complex was first dissolved in 5 mL of 2 M KOH solution. To this were added 5 mg of solid potassium persulfate and 1 ml of 5% sodium hypochlorite solution. The resulting golden solution was heated just below boiling for 10 min, then allowed to cool to room temperature. The solution was then diluted with water to 25 mL in a volumetric flask. Ruthenium concentration was determined by measuring the