Mechanism of Tertiary Phosphine Catalyzed Isomerization of Tetragonal Planar Platinum(II) Complexes

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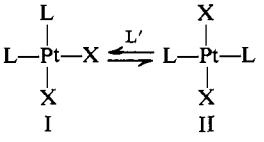
Abstract: The tertiary phosphine catalysis of phosphine ligand exchange reactions and cis–trans isomerization reactions in complexes of the type *cis*-$[PtX_2L_2]$ (X = Cl, I; L = Me_2PhP, *o*-$CH_3C_6H_4Me_2P$) and the thermodynamic stabilities of the complexes $[PtX_2LL']$ relative to $[PtX_2L_2]$ and $[PtX_2L'_2]$ (L' = Me_2PhP, $(p\text{-}CH_3C_6H_4)_3P$, $n\text{-}Bu_3P$) have been investigated by nmr spectroscopy. The results obtained fully substantiate a consecutive displacement mechanism for cis–trans isomerization *via* an ionic intermediate $[PtXL_3]^+X^-$. Previously reported results concerning solvent effects on the rate of cis–trans isomerization have been reinterpreted in terms of a consecutive displacement mechanism. Uv kinetic studies of Me_2PhP catalyzed trans to cis isomerization of $[PtI_2(Me_2PhP)_2]$ have shown the rate to be zero order in platinum complex and second order in added Me_2PhP concentration. At 38° a second-order rate constant of 2.08×10^4 l. mol^{-1} min^{-1} was observed.

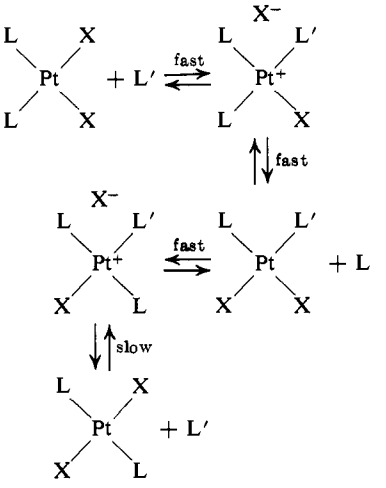
In recent communications Haake and Pfeiffer[1,2] have reported spectrophotometric studies of the tertiary phosphine (L') catalyzed cis–trans isomerization of tetragonal planar bis(trialkylphosphine)-dichloroplatinum(II) complexes {I and II: L = $(n\text{-}C_3H_7)_3P$, $(n\text{-}C_4H_9)_3P$; X = Cl; L' = $(n\text{-}C_3H_7)_3P$, $(n\text{-}C_4H_9)_3P$, $(n\text{-}C_4H_9)Ph_2P$} (eq 1). On addition of



(1)

catalytic amounts of L' to 10^{-4} *M* cyclohexane solutions of I (L' = L or L' ≠ L), well-behaved first-order rates were observed. For a given L, variation of the concentration of L' gave a second-order rate constant characteristic of a particular L'. The data were analyzed in the following way.[1] "Since the total amount of L is greater by at least a factor of 20 than L', exchange of L and L' would lead to either (1) curved plots if the rate of exchange were comparable to the rate of isomerization or (2) nearly identical rates for the isomerization of I {L = $(n\text{-}C_3H_7)_3P$} by $(n\text{-}C_3H_7)_3P$ and $(n\text{-}C_4H_9)_3P$ if exchange were rapid compared to isomerization. Consequently, *isomerization must proceed much faster than exchange; the phosphines do not mix during isomerization.*" This conclusion, which is based on assumption 2 (above), is clearly not compatible with the previously proposed[3-5] displacement mechanism outlined in Scheme I which requires two consecutive ligand substitutions to effect cis–trans isomerization. The rate of isomerization exhibits a marked solvent dependence[2,6] being slower in more polar solvents. Haake and Pfeiffer suggest that these observations do not favor the consecutive displacement mechanism for isomerization which requires formation of $[L_2L''PtX]^+X^-$ as an intermediate[3] since formation

Scheme I. Consecutive Displacement Mechanism for L' Catalyzed Cis–Trans Isomerization of $[PtX_2L_2]$



of ionic species should be favored by polar solvents. Haake and Pfeiffer have proposed that the L' catalyzed isomerization of $[PtCl_2L_2]$ involves pseudorotation of a pentacoordinate intermediate in which L' remains stereochemically unique.[1,2]

The anticipation of curved plots, if the rate of ligand exchange were comparable to isomerization, seems reasonable ((1) above). However, anticipation of nearly identical rates of isomerization for various L' if ligand substitution occurs more rapidly than isomerization ((2) above) is speculative. Assumption 2 would in fact only be realized for one of the following conditions. (3) If the catalytic efficiencies of free L and L' are similar and the mixed species $[PtX_2LL']$ is at least as thermodynamically stable as its $[PtX_2L_2]$ analog, assumption 2 will be correct. (4) If the catalytic efficiency of L' for the isomerization is much greater than that of L, then assumption 2 will only be correct when the thermodynamic stability of $[PtX_2LL']$ is much greater than that of $[PtX_2L_2]$ (*i.e.*, no free L' present in solution). If neither (3) nor (4) is operative in the system L'–$[PtX_2L_2]$, then assumption 2 and the conclusion used to eliminate the consecutive displacement mechanism—that isomerization must proceed *much faster* than phosphine exchange—will not be valid. We here report ^1H nmr

(1) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 92, 4996 (1970).
(2) P. Haake and R. M. Pfeiffer, *Chem. Commun.*, 1330 (1969).
(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter V.
(4) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1966.
(5) L. Cattalini and M. Martelli, *J. Amer. Chem. Soc.*, 91, 312 (1969).
(6) P. Haake and R. M. Pfeiffer, *ibid.*, 92, 5243 (1970).

Table I. ^{1}H Nmr Data for Some Tertiary Phosphine Platinum(II) Halogen Complexes in $CDCl_3$ Solution (35°)[a]

	Phosphine methyl protons						o-Tolyl methyl protons
	Phosphine trans to halogen (1:1 doublet)[7]			Phosphine trans to phosphine (1:2:1 triplet)[7]			
	δ	J_P	$J_{^{195}Pt}$	δ	J_P	$J_{^{195}Pt}$	
cis-$[PtCl_2(Me_2PhP)_2]$[7]	1.78	11.1	34.9				
cis-$[PtI_2(Me_2PhP)_2]$[7]	1.91	10.5	35.8				
trans-$[PtI_2(Me_2PhP)_2]$[7]				2.18	3.6	25.4	
cis-$[PtCl_2(Me_2$-*o*-$CH_3C_6H_4P)_2]$[b,f]	1.61	11.1	33.4				2.85
$[PtCl(Me_2PhP)_3]^+Cl^-$ [c]	1.54	10.8	41	2.01	4.1	23	
	(1.50)	(11.1)	(40.5)	(1.83)	(4.2)	(23.5)	
$[PtI(Me_2PhP)_3]^+I^-$ [d]	1.96	10.8	42	2.46	3.9	24	
$[PtCl(Me_2PhP)_3]^+PF_6^-$	1.44	10.9	40	1.93	3.8	24	
$PtCl_2(Me_2$-*o*-$CH_3C_6H_4P)(Me_2PhP)$[e,f]							1.76
$PtCl_2(Me_2$-*o*-$CH_3C_6H_4P)((p$-$CH_3C_6H_4)_3P)$[e]							3.01

[a] Chemical shifts (δ) ±0.01 ppm, coupling constants (J) ±0.2 Hz. [b] On the addition of free phosphine (<1%) the trans isomer was observed (1:2:1 triplet at δ 1.8; <5% at equilibrium). [c] Spectrum recorded at −10°. Figures in parentheses are the data obtained in MeOH solution at 35°. [d] Spectrum only poorly resolved at −60°. Data obtained from a mixture of $[PtI_2(Me_2PhP)_2]$ and Me_2PhP (*ca.* 3:2) at 0°. [e] Phosphine methyl proton resonances of mixed species $[PtCl_2LL']$ cannot be assigned unambiguously owing to overlap with phosphine methyl resonances of $[PtCl_2L_2]$ and $[PtCl_2L_2']$ though resonances of the phosphine methyl protons of mixed ligand complexes are observed. [f] $CH_3C_6H_4$ = tolyl.

studies of tertiary phosphine catalyzed ligand exchange in the complexes $[PtX_2(Me_2PhP)_2]$ (X = Cl, I) which show the conclusion "that isomerization must proceed much faster than phosphine exchange" to be erroneous. Furthermore the nmr studies provide considerable supporting evidence in favor of the consecutive displacement mechanism for cis–trans isomerization (Scheme I). As such we have carried out a uv kinetic study of the Me_2PhP catalyzed trans to cis isomerization of $[PtI_2(Me_2PhP)_2]$ in MeOH. The data obtained together with that previously reported for tertiary phosphine catalyzed cis to trans isomerization reactions in cyclohexane are interpreted in terms of the consecutive displacement mechanism for isomerization.

Experimental Section

Preparation of Compounds. Complexes of the type $[PtX_2L_2]$ were prepared using the general procedures described by Jenkins and Shaw.[7] The following new compounds were prepared.

***cis*-Dichlorobis(dimethyl-*o*-tolylphosphine)platinum(II).** White plates were obtained in 27% yield, mp 214–220°. The ^{1}H nmr spectrum of this product in $CHCl_3$ indicated the presence of a small amount (<5%) of the trans isomer. *Anal.* Calcd for $C_{18}H_{26}Cl_2P_2Pt$: C, 37.89; H, 4.56. Found: C, 37.85; H, 4.55.

Chlorotris(dimethylphenylphosphine)platinum(II) Hexafluorophosphate. *cis*-Dichlorobis(dimethylphenylphosphine)platinum(II) (0.06 g) was dissolved in $CHCl_3$ (10 ml), Me_2PhP (0.015 g) and excess ammonium hexafluorophosphate (1.0 g) were added, and the mixture was shaken for 3 days. Filtration and evaporation of the filtrate gave a solid residue which recrystallized from chloroform–hexane as yellow microprisms, 40%, mp 55–65°. *Anal.* Calcd for $C_{24}H_{33}ClF_6P_4Pt$: C, 36.5; H, 4.28. Found: C, 37.16; H, 4.43. Recrystallization from dichloromethane–diethyl ether gave pale yellow microprisms, mp 64–67°.

Attempts to prepare an analytically pure sample of iodotris(dimethylphenylphosphine)platinum(II) hexafluorophosphate from the diiodo complex and either NH_4PF_6 or $AgPF_6$ were unsuccessful.

Separation of Cis and Trans Isomers of Diiodobis(dimethylphenylphosphine)platinum(II). A cis–trans mixture of diiodobis(dimethylphenylphosphine)platinum(II)[7] (2 g) was extracted with refluxing cyclohexane (3 × 25 ml). The combined cyclohexane extracts were filtered and evaporated to dryness. The resultant solid recrystallized from methylene chloride–petroleum ether (bp 30–60°) to yield *trans*-diiodobis(dimethylphenylphosphine)platinum(II) as orange plates (1.24 g), mp 139–142° (sample melts then recrystallizes in the cis form which then melts at 170–174°). The product was identified as the trans isomer from its ^{1}H nmr spectrum.

The residue remaining after cyclohexane extraction recrystallized from methylene chloride–petroleum ether (bp 30–60°) to yield *cis*-diiodobis(dimethylphenylphosphine)platinum(II) as yellow prisms (0.30 g), mp 170–173°. The product was identified as the cis isomer from its ^{1}H nmr spectrum.

Spectroscopic Studies. ^{1}H nmr spectra were recorded on a Varian A56/60D spectrometer. Infrared spectra were recorded on a Perkin-Elmer 180 spectrometer.

Uv spectra were recorded on a Bausch and Lomb Spectronic 505 at 38°. *trans*-$[PtI_2(Me_2PhP)_2]$ was recrystallized three times from chloroform–cyclohexane and dried under vacuum at 30° for 24 hr prior to use in kinetic runs. The Me_2PhP used was redistilled just prior to kinetic runs and all manipulations involving Me_2PhP were carried out under an atmosphere of nitrogen. In order to minimize oxidation of phosphine by dissolved oxygen, uv spectroscopic solvents were purged with O_2 free dry nitrogen for 3 hr prior to use.

Solid samples were dissolved in one part ACS Spectranalyzed chloroform (by volume) and 19 parts ACS methanol (38°) added. The observed maxima were the following: *cis*-$[PtI_2(Me_2PhP)_2]$, 352 mμ (ε 2.50 × 10^3); *trans*-$[PtI_2(Me_2PhP)_2]$, 288 mμ (ε 4.70 × 10^3), 332 mμ (ε 2.40 × 10^3). The solutions used for the kinetic studies of trans to cis isomerization of $[PtI_2(Me_2PhP)_2]$ were 4 × 10^{-4} M in complex. The reaction was monitored at 332 mμ and exhibited a sharp isobestic point at 344 mμ.

Results and Discussion

Proton Nmr Studies of Phosphine Ligand Exchange in the Complexes $[PtX_2(Me_2PhP)_2]$. Addition of one Me_2PhP per Pt atom to a $CDCl_3$ solution of *cis*-$[PtCl_2(Me_2PhP)_2]$ (0.2 M) at *ca.* −10° gives a proton nmr spectrum containing a basic 1:2:1 triplet resonance (excluding ^{195}Pt coupling) assignable to two *trans*-Me_2PhP ligands and a doublet resonance assignable to a *cis*-Me_2PhP ligand (see Table I). No resonances assignable to free Me_2PhP are observed. A similar pattern is obtained at 35° in MeOH solution. The spectra are consistent with the solution species being $[PtCl(Me_2PhP)_3]^+Cl^-$, and on addition of NH_4PF_6 to such solutions the salt $[PtCl(Me_2PhP)_3]^+PF_6^-$ is readily isolated and structurally characterized (see Table I for nmr data). The far-infrared spectrum of a 0.1 M chloroform solution of *cis*-$[PtCl_2(Me_2PhP)_2]$ in the presence of one Me_2PhP per Pt further confirms the formation of $[PtCl(Me_2PhP)_3]^+Cl^-$ (see Table II). In the range 500–250 cm^{-1} the spectrum contains only one absorption assignable to a ν(Pt–Cl) band and is identical with the far-infrared spectrum of $[PtCl(Me_2PhP)_3]^+PF_6^-$. Thus in $CDCl_3$ solution in the temperature range −10 to 31° eq 2 lies well to the right-hand side. Previous conductivity studies[8] have confirmed the for-

(7) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).

(8) S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 6, 1133 (1967).

Table II. Far-Infrared Data for Representative Phenyldimethylphosphine Complexes[a]

Complex	Far-ir absorptions (500–250 cm^{-1})
cis-$[PtCl_2(Me_2PhP)_2]$	490 vs, 457 s, 437 s, 425 w, 316 vs, 292 vs
$[PtCl(Me_2PhP)_3]^+PF_6^-$	490 vs, 450 s, 434 s, 424 s, 303 vs
$[PtCl(Me_2PhP)_3]^+Cl^-$	488 vs, 450 s, 434 s, 424 s, 303 vs

[a] Spectra are recorded in 0.1 *M* $CHCl_3$ solutions at 31°; ν(Pt–Cl) values are underlined. Weak absorptions in the range 355–380 cm^{-1} could not be observed due to incompletely compensated $CHCl_3$ bands.

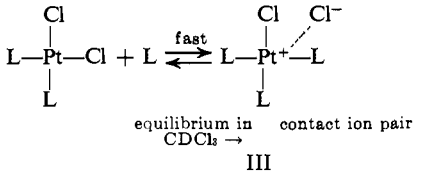
mation of $[PtCl(PrPh_2P)_3]^+Cl^-$ when $PrPh_2P$ is added to a CH_2Cl_2 solution of $[PtCl_2(PrPh_2P)_2]$.

On warming a $CDCl_3$ solution of $[PtCl(Me_2PhP)_3]^+Cl^-$ to 20° the cis doublet and trans triplet resonances coalesce to a broad singlet. Loss of ^{195}Pt coupling indicates that rapid intermolecular exchange of Me_2PhP ligands is occurring.[9-13] In the region of coalescence the methyl proton line shape is insensitive to a tenfold dilution suggesting that an intramolecular process is probably the rate-determining step of ligand exchange. Since collapse of the methyl protons is not observed for the corresponding hexafluorophosphate salt even at 47°, it is most probable that Cl^- substitution of Me_2PhP trans to Me_2PhP in $[PtCl(Me_2PhP)_3]^+Cl^-$ is the rate-determining step for Me_2PhP ligand exchange. Since, in the concentration range 0.2–0.02 *M*, this exchange is insensitive to concentration, it is probable that the species $[PtCl(Me_2PhP)_3]^+Cl^-$ exists mainly as a contact ion pair and/or a square-pyramidal species with a chloride ligand occupying the axial position and only weakly bound to the central platinum (*i.e.*, structure III). The addition of a small amount of MeOH (*ca.* 5% by volume) to a $CDCl_3$ solution of $[PtCl(Me_2PhP)_3]^+Cl^-$ at 35° completely inhibits the Me_2PhP exchange process. However, if excess chloride ion in the form of $[AsPh_4]^+Cl^-$ is now added to this solution, the methyl proton resonances again collapse and coalesce. We attribute the inhibiting effect of MeOH to solvation of the contact ion pair (III). This results in the removal of the Cl^- anion from an axial coordination site thereby preventing rapid substitution of coordinated Me_2PhP by Cl^-, *i.e.*

$$[PtCl(Me_2PhP)_3]^+Cl^- \overset{MeOH}{\rightleftharpoons} [PtCl(Me_2PhP)_3]^+(MeOH)_x + Cl^-(MeOH)_y$$

Addition of excess Cl^- to this system increases the concentration of the contact ion pair and thereby promotes Me_2PhP ligand exchange.

When Me_2PhP is added to $CDCl_3$ solutions of *cis*-$[PtCl_2(Me_2PhP)_2]$ at added Me_2PhP to complex ratios of 0.5:1, the low-temperature nmr shows the presence of *ca.* equal amounts of cis complex and chloride salt in the solution and no free Me_2PhP. 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 (eq 2). In $CDCl_3$ and for L = Me_2PhP, eq 2 lies well



(2)

to the right-hand side and the concentration of free L is small. The choice of these substitution pathways is consistent with the known strong trans effects exhibited by tertiary phosphine ligands.

The nmr spectrum of equal amounts of *cis*-$[PtCl_2(Me_2PhP)_2]$ and $[PtCl(Me_2PhP)_3]^+PF_6^-$ 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 Me_2PhP. Addition of $[AsPh_4]^+Cl^-$ to the solution collapses the methyl proton resonances.

When 5% Me_2PhP per Pt is added to an equilibrium mixture of *cis*- and *trans*-$[PtI_2(Me_2PhP)_2]$ in $CDCl_3$ at 0° (*ca.* 25% cis, 75% trans) formation of the salt $[PtI(Me_2PhP)_3]^+I^-$ occurs as evidenced by ^1H nmr studies (see Table I and Figure 1). On warming this solution, collapse and coalescence of salt and cis isomer methyl resonances with concurrent loss of ^{195}Pt coupling ($J_{^{195}Pt-H}$ = 35.8 Hz) for cis isomer occur *prior* to collapse and loss of ^{195}Pt coupling for the trans isomer resonances ($J_{^{195}Pt-H}$ = 25.4 Hz) (see Figure 1B and C). This indicates that Me_2PhP ligand exchange between *cis*-$[PtI_2(Me_2PhP)_2]$ and $[PtI(Me_2PhP)_3]^+I^-$ is occurring faster than ligand exchange in *trans*-$[PtI_2(Me_2PhP)_2]$ and faster than cis–trans isomerization.[10,13] Thus the previously reported conclusion "that isomerization must proceed *much faster* than phosphine exchange"[1,2] is clearly not the case for Me_2PhP–platinum(II) complexes.[14] Intuitively, the same is probably true for the complexes previously studied by Haake and Pfeiffer.[1,2]

From the nmr data in Figure 1, it can be concluded that MePhP substitution of I trans to Me_2PhP in *cis*-$[PtI_2(Me_2PhP)_2]$ and the reverse process (I^- substitution of Me_2PhP trans to Me_2PhP in $[PtI(Me_2PhP)_3]^+$) occur faster than Me_2PhP substitution of either I trans to I or Me_2PhP trans to Me_2PhP in *trans*-$[PtI_2(Me_2PhP)_2]$. This is consistent with known ligand trans effects. At higher temperatures Me_2PhP ligand exchange in *trans*-$[PtI_2(Me_2PhP)_2]$ is seen to occur (Figure 1D and 1E). A lower coalescence temperature indicates that ligand exchange in the iodide system is more labile than in the chloride analog. In the region of coalescence the methyl proton line shape of the iodide system is insensitive to a tenfold dilution.

Collapse of the methyl proton resonance spectrum of *cis*-$[PtI_2(Me_2PhP)_2]$ prior to collapse of the trans triplet resonances is also observed when the added ligand L′ = Ph_3P, *n*-Bu_3P, (*o*-$CH_3C_6H_4)Me_2P$, (*o*-$CH_3C_6H_4)_2MeP$, and Me_2PhAs. Ligands such as Ph_3As and pyridine do not cause collapse of the methyl resonances at 35°.

The Relative Thermodynamic Stabilities of the Complexes PtX_2L_2 and PtX_2LL'. The observation of dif-

(9) The collapse or broadening of phosphine methyl proton nmr spectra on addition of excess tertiary phosphine has been previously reported for tetragonal-planar d^8 complexes of Pd(II),[10] Ir(I),[11] and Rh(I)[12,13] containing MeR_2P ligands.

(10) J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, 91, 1941 (1969).

(11) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 2705 (1970).

(12) A. J. Deeming and B. L. Shaw, *ibid.*, 597 (1969).

(13) J. P. Fackler, *Inorg. Chem.*, 9, 2625 (1970).

(14) If cis–trans isomerization was much faster than ligand exchange then the methyl proton resonances of the cis and trans isomers would have coalesced without loss of ^{195}Pt coupling.

ferent second-order rate constants for eq 1, characteristic of a particular L′, should be determined in part by the relative thermodynamic stabilities of mixed-ligand species such as $[PtX_2LL']$ (see the introductory section, points 3 and 4).

When an equimolar mixture of *cis*-$[PtCl_2(Me_2PhP)_2]$ and *cis*-$[PtCl_2((o\text{-}CH_3C_6H_4)Me_2P)_2]$ in $CDCl_3$ is allowed to stand at 20° for 2 days a new, low-intensity resonance pattern assignable to the mixed-ligand complex *cis*-$[PtCl_2(Me_2PhP)((o\text{-}CH_3C_6H_4)Me_2P)]$ is observed. If a trace of free Me_2PhP (less than 1% relative to complex concentration) is added to the mixture, the rate of formation of the mixed-ligand complex is markedly enhanced and an equilibrium situation (eq 3, L = Me_2PhP) is established within 15–20 min. The mixed species (IV, L = Me_2PhP) is easily discernible in the nmr by a new singlet resonance assignable to the *o*-tolylmethyl protons of IV (see Table I). The value of *K*, the equilibrium constant, may be obtained by integration of the nmr spectrum. From four observations recorded at differing concentrations and complex ratios a value for *K* of 2.5 ± 0.3 (T = 35°) is obtained. If the ligand distribution in this system were statistical the value of *K* would be 4.0. A similar study on equilibrium mixtures of *cis*-$[PtCl_2((o\text{-}CH_3C_6H_4)Me_2P)_2]$ and $[PtCl_2((p\text{-}CH_3C_6H_4)_3P)_2]$ gave a value for *K* of 1.9 ± 0.3 (T = 35°). The nmr spectra of mixtures of *cis*-$[PtCl_2((o\text{-}CH_3C_6H_4)Me_2P)_2]$ and $[PtCl_2(n\text{-}Bu_3P)_2]$ in $CDCl_3$ (−60 to 35°) in the presence of trace amounts of free Me_2PhP or $n\text{-}Bu_3P$ gave no new proton resonances suggesting that the concentration of a mixed-ligand species such as IV (L = $n\text{-}Bu_3P$) must be small. These results indicate not unexpectedly that the thermodynamic stability of mixed species such as $[PtX_2LL']$, relative to $[PtX_2L_2]$ or $[PtX_2L'_2]$, is dependent on the nature of L and L′ and, as in the case of IV (L = $n\text{-}Bu_3P$), the mixed species may be considerably less stable. Consequently anticipation of nearly identical rates of cis to trans isomerization of $[PtX_2L_2]$ for different L′ catalysts if ligand exchange is rapid compared to isomerization (see introductory section, assumption 2) is not a valid assumption for $[PtX_2L_2]/[L']$ systems.

$$cis\text{-}[PtCl_2L_2] + cis\text{-}[PtCl_2((o\text{-}CH_3C_6H_4)Me_2P)_2] \overset{K}{\rightleftharpoons} \underset{\text{IV}}{cis\text{-}[PtCl_2L((o\text{-}CH_3C_6H_4)Me_2P)]} \quad (3)$$

The above nmr data do not disprove pseudorotation of a five-coordinate intermediate as the mechanism of L′ catalyzed cis–trans isomerization of $[PtX_2L_2]$. However these studies clearly show that the arguments used to eliminate the consecutive displacement mechanism[1,2] are *not* correct. Furthermore the observations that addition of Me_2PhP to $[PtI_2(Me_2PhP)_2]$ readily generates the salt $[PtI(Me_2PhP)_3]^+I^-$ and that Me_2PhP ligand exchange between the salt and the cis isomer is fast are fully consistent with the consecutive displacement mechanism for isomerization. In contrast an isomerization process which is faster than ligand substitution would prevent the observation of trans effects. Trans effects are generally characteristic of the reactions of square-planar complexes of platinum(II).

A Reanalysis of Previously Reported Kinetic Data in Terms of a Consecutive Displacement Mechanism of Cis–Trans Isomerization. The proton nmr studies of $[PtCl(Me_2PhP)_3]^+Cl^-$ in $CHCl_3$ and MeOH suggest that the rate-determining step for isomerization of the cis isomer (I) to the trans isomer (II) is substitution of L (or L′) trans to X in the ion pair $[PtXL_3]^+X^-$ by X^-. For the reverse process substitution of X trans to X in *trans*-$[PtX_2L_2]$ (II) by L (or L′) will be rate determining. Choice of these rate determining steps in the consecutive displacement mechanism is consistent with known trans effects *and* the second-order rate constants observed by Haake and Pfeiffer.[1,2] In nonpolar solvents such as cyclohexane one would anticipate that the concentration of ionic species of the type $[PtXL_2L']^+X^-$ and $[PtXL_3]^+X^-$ would be small and furthermore that these salts would exist primarily as contact ion pairs. As such, the total concentration of salt would be di-

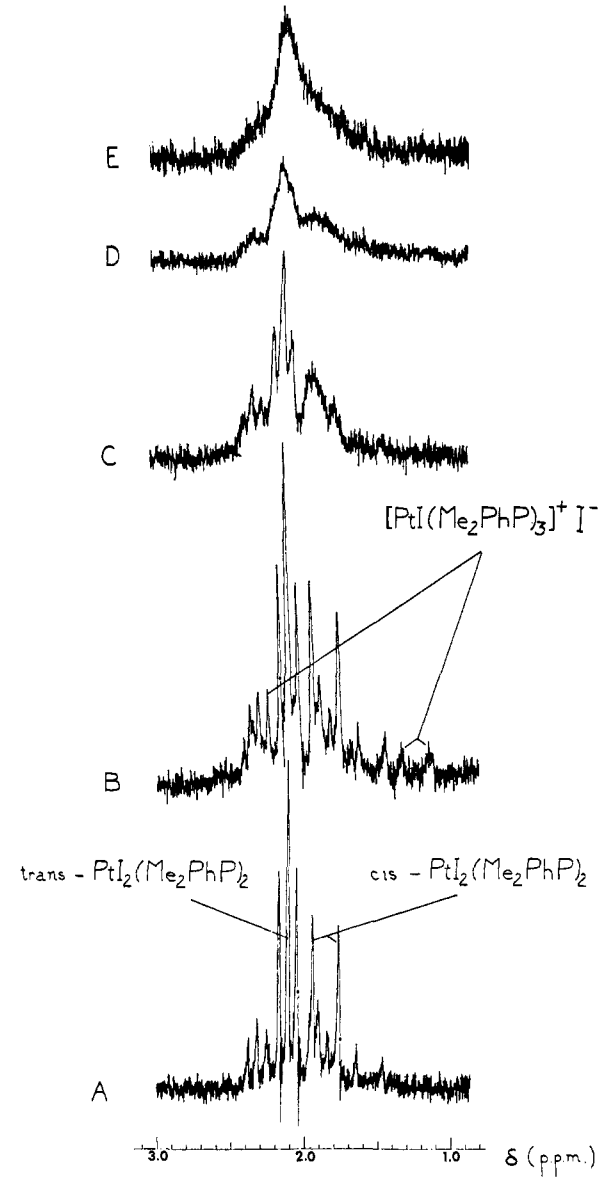


Figure 1. The variable-temperature ^1H nmr spectra of a cis–trans mixture of $[PtI_2(Me_2PhP)_2]$ in $CDCl_3$ solution: (A) at 35° (the high-field ^{195}Pt 1:2:1 triplet and low-field ^{195}Pt 1:1 doublet resonances are masked by partial overlap with the major resonances), (B) at 0° in the presence of a *ca.* 5% molar ratio of added Me_2PhP (the resonances assigned to $[PtI(Me_2PhP)_3]^+I^-$ are more easily identified by addition of *ca.* 50–100% Me_2PhP), (C) at 20° in presence of 5% Me_2PhP, (D) at 30° in presence of 5% Me_2PhP, (E) at 40° in presence of 5% Me_2PhP.

rectly proportional to the amount of added L′, and hence the rate-determining step for cis to trans isomerization in cyclohexane will be first order in added L′. Different L′ will give different second-order rate constants owing to (5) changes in the thermodynamic stabilities of mixed species, such as IV and $[PtXL_2L']^+X^-$, relative to their unmixed analogs (this will also determine the overall concentrations of free L and L′); and (6) the relative catalytic efficiencies of various L′ (*i.e.*, the ease with which L′ in $[PtXL_2L']^+X^-$ is substituted by X^-).

Role of Solvent in the Mechanism of Cis–Trans Isomerization. Haake and Pfeiffer[2,6] have shown that addition of small aliquots of polar solvents (S) such as chloroform or nitromethane to cyclohexane solutions of *cis*-$PtCl_2(n\text{-}Bu_3P)_2$ markedly inhibits the *n*-Bu_3P catalyzed isomerization to the trans isomer. The observed second-order rate constants, k_0, for cis to trans isomerization were found to be dependent on the concentration of added polar solvent (S) according to the following expression[6]

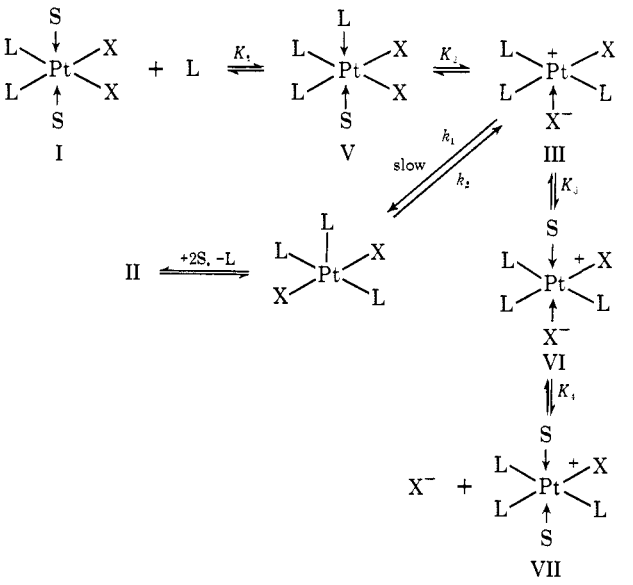
$$\frac{1}{k_0} = \frac{1}{k_h} + K[S]^n/k_h \qquad (4)$$

where k_h = second-order rate constant in neat cyclohexane and k_0 = observed second order rate constant for various concentrations of added polar solvents (S) at a fixed concentration of added *n*-Bu_3P. For S = nitromethane, acetonitrile, diethyl ether, and chloroform, linear plots were obtained for $n = 1$. For S = MeOH, linear plots were obtained for $n = 2$. From these results it is clear that association of solvent molecules with a platinum complex is occurring in the systems $[PtX_2L_2]$–L–polar solvent, an observation that is further supported by our nmr studies of Me_2PhP ligand exchange in $[PtX_2(Me_2PhP)_2]$ in $CDCl_3$ and MeOH solutions. The kinetic data appertaining to solvent effects[6] may be incorporated into the consecutive displacement mechanism for isomerization in the following way. It is reasonable to assume that solvation of the platinum(II) complexes will result in octahedral species. Axial solvation positions (weak bonding to Pt) may be occupied by S, L, and/or X^-. The cis complex may exist in the disolvated form I or as V in which one solvent molecule has been replaced by the added ligand L (see Scheme II). The contact ion pair $[PtXL_3]^+X^-$ (III), for which we have earlier postulated a square-pyramidal structure, will, in the presence of an added polar solvent, tend to adopt the octahedral, solvated structure VI in which one S molecule occupies the sixth site. In VI SN2 substitution of L by X^- cannot occur as S will block the leaving group L. If the added solvent S has reasonably good ligand properties, and remembering that $[S] \gg [X^-]$, it is possible that the axial X^- in VI may be substituted by a molecule of S to give the disolvated cation VII. Since substitution of L trans to X in III by X^- is rate determining, the following kinetic equations, based on Scheme II, may be derived for cis to trans isomerization

$$\text{rate} = \frac{d[II]}{dt} = k_1[III] - k_2[II][L] \qquad (5)$$

Equilibria involving I, III, V, VI, and VII have been shown, or can be assumed on the basis of known relative trans effects, to be rapidly established. Also the

Scheme II. Kinetic Scheme for L Catalyzed Cis to Trans Isomerization of $[PtX_2L_2]$ in Cyclohexane in the Presence of Small Quantities ($\leq 10^{-2}$ *M*) of Added Polar Solvent (S)



cis to trans isomerization goes to completion in cyclohexane,[1,2] and k_2 can be considered to be *ca.* 0. If [total Pt complex] − [II] = [C], then [C] = [I] + [III] + [V] + [VI] + [VII], *i.e.*

$$[C] = [III]\left\{\frac{[S]^2}{K_1K_2[L]} + 1 + \frac{[S]}{K_2} + K_3[S] + \frac{K_3K_4[S]^2}{[X^-]}\right\} \qquad (6)$$

From eq 5 and 6

$$\frac{d[II]}{dt} = k_1[C]\Big/\left\{\frac{[S]^2}{K_1K_2[L]} + 1 + \frac{[S]}{K_2} + K_3[S] + \frac{K_3K_4[S]^2}{[X^-]}\right\} \qquad (7)$$

Since the addition of small quantities of CH_3NO_2, $CHCl_3$, etc. (*ca.* 10^{-2} *M*) to cyclohexane will have very little effect on the dielectric constant of the total solvent and remembering that the previously reported data[6] are for the conditions 10^{-2} $M \approx [S] > [Pt\ complex] \gg [L_0]$ (= total concentration of added ligand), one can make the assumption that the total concentration of III and ionic species VI and VII is very small relative to the total concentration of I and V, *i.e.*, $1/K_1K_2 \gg K_3K_4$. Furthermore one would anticipate from crystal field stabilization energy considerations[3] that $K_1 \gg K_2$. Since X^- has better solvating ability toward Pt than S (CH_3NO_2, $CHCl_3$, etc.), $K_3 > K_4$. (This is supported by our nmr studies of Cl^- promoted Me_2PhP exchange in $[PtCl(Me_2PhP)_3]^+Cl^-$ in $CHCl_3$ solution.) As [S] ≪ 1 it follows that $[S] \gg [S]^2$. Under these conditions eq 7 simplifies to

$$\frac{d[II]}{dt} = k_1[C]/\{1 + [S](1/K_2 + K_3)\} \qquad (8)$$

under the conditions applicable to eq 8, $[C] \approx [I]$, *i.e.*

$$\frac{d[II]}{dt} = -\frac{d[I]}{dt} = k_0[C] \qquad (9)$$

From eq 8 and 9

$$\frac{1}{k_0} = \frac{1}{k_1} + \frac{[S]}{k_1}(1/K_2 + K_3) \qquad (10)$$

Equation 10 has the same format as eq 4 reported by Haake and Pfeiffer[6] ($k_h = k_1$; $K = (1/K_2 + K_3)$. By plotting $\log[(1/k_0) - (1/k_h)]$ *vs.* [S], a slope of unity was obtained.[6] Under the conditions applicable to eq 8 and 9, [III] = K_2[V]/[S] ([V] ≪ [I]). For standard solvent conditions, [S] is a constant. In nonpolar solvents where the concentration of ionic species is very small, most of the added ligand will probably be present in an unassociated form or as V. When initial [I] is constant, [V] will exhibit a first-order dependence on the concentration of added ligand [L_0]. Thus eq 5 may be rewritten in the form

$$\text{rate} = -\frac{d[I]}{dt} = \frac{d[II]}{dt} = k_0'[I][L_0] \qquad (11)$$

That is to say that the rate of cis to trans isomerization in nonpolar solvents will exhibit a first-order dependence on [I] and a first-order dependence on [L_0] which is consistent with experimental observations.[1,2,6] For most of the added solvents studied the rate of cis to trans isomerization exhibited an inverse dependence on the concentration of S.[6] However, when methanol was the added solvent an inverse second-order dependence on methanol concentration was observed.[6] This is probably due to the fact that MeOH has better solvating properties. As such, it is probable that the effect of added MeOH, relative to S = CH_3NO_2 or $CHCl_3$, is to decrease K_1 (decreases concentration of V) and to increase the concentrations of the ionic species VI and VII (*i.e.*, K_3 and K_4 increase). Since MeOH inhibits Cl^- substitution of Me_2PhP in $[PtCl(Me_2PhP)_3]^+$-Cl^-, it is possible that VII (S = MeOH) is the major ionic species present. Under these conditions the $[S]^2$ terms in eq 7 would become predominant.

The analysis so far has been based on the assumption that, in cyclohexane, most of the added phosphine catalyst (L) will be present in the unassociated form and that ionic species such as VI and VII will be present only in very small amounts. However, as our nmr studies in $CDCl_3$ and MeOH have shown, replacement of cyclohexane by solvents with greater dielectric constants stabilizes the ionic intermediates VI and VII with the result that, for a fixed amount of added L, salt concentrations will increase and the concentration of free L will *decrease*. Stabilization of the salts by polar solvents will increase the free energy of activation for substitution of coordinated L (or L′) by X^-. In bulk polar solvents such as methanol the cis isomer of the complexes $[PtX_2L_2]$ is thermodynamically preferred.[15] For trans to cis isomerization, where the rate-determining step is substitution of X trans to X in II by L, the stabilization of the ionic species will result in a decrease in the concentration of free L and hence bulk polar solvents will inhibit the rate. On the assumption that for bulk solvent such as MeOH most of the added L will be in the form of the disolvated ionic species VII (supported by our nmr studies), the following kinetic data for trans to cis isomerization based on the simplified reaction paths outlined in Scheme III may be derived.

(15) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 525 (1956).

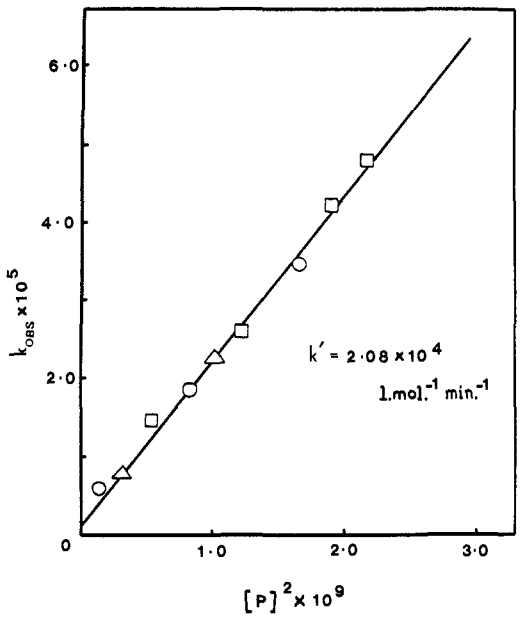
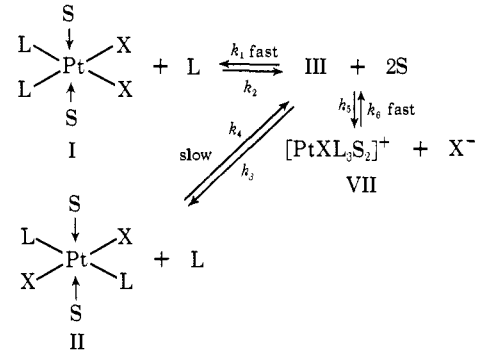


Figure 2. Plot of pseudo-first-order rate constants k_{obsd} *vs.* square of added Me_2PhP concentration $[P]^2$ for Me_2PhP catalyzed trans to cis isomerization of $[PtI_2(Me_2PhP)_2]$ in MeOH solution at 38°. (○, △, and □ represent different preparations of *trans*-$[PtI_2(Me_2PhP)_2]$; k' = second-order rate constant, the average deviation of which, as determined by least squares analysis, is 0.12 × 10^4 l. mol^{-1} min^{-1}.) The intercept value of 0.22 × 10^{-5} mol l.$^{-1}$ min^{-1} represents methanol catalyzed trans to cis isomerization. A solution of *trans*-$[PtI_2(Me_2PhP)_2]$ in MeOH at 38°, in the absence of any added Me_2PhP, slowly isomerizes to the cis isomer over a period of *ca.* 24 hr.

Scheme III. Kinetic Scheme for L Catalyzed Trans to Cis Isomerization of $[PtX_2L_2]$ in a Polar Solvent (*e.g.*, S = MeOH)



$$\text{rate} = \frac{d[I]}{dt} = k_1[III] - k_2[I][L] \qquad (12)$$

As the first step is slow (*i.e.*, k_4 is small) and the remaining steps are fast, the steady-state approximation may be applied. For complete trans to cis isomerization $k_3 \approx 0$. Thus

$$\frac{d[III]}{dt} = k_2[I][L] + k_6[VII][X^-] - k_1[III][S]^2 - k_5[III][S]^2 \qquad (13)$$

Rearranging eq 13 and substituting into eq 12 for [III]

$$\frac{d[I]}{dt} = \frac{k_1k_2[I][L]}{[S]^2(k_1 + k_5)} + \frac{k_1k_6[VII][X^-]}{[S]^2(k_1 + k_5)} - k_2[I][L] \qquad (14)$$

For MeOH bulk solvent $[S]^2$ is constant. For L = Me_2PhP, [VII] and $[X^-]$ are approximately equal to the concentration of added ligand [L_0], *i.e.*, the free ligand

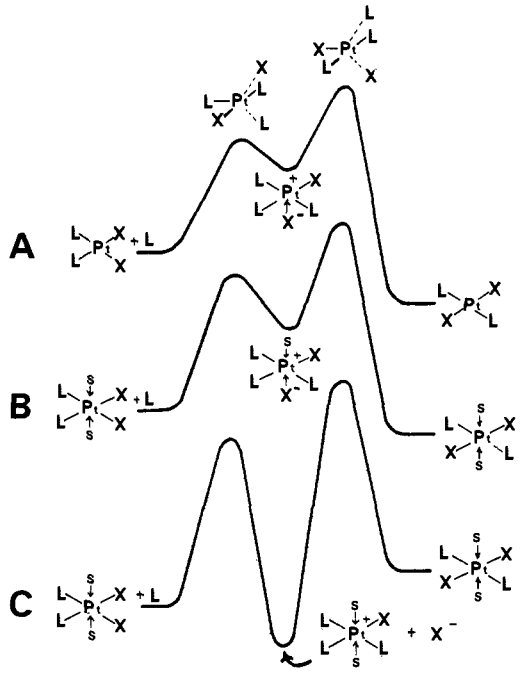


Figure 3. Qualitative potential energy profiles for L catalyzed cis–trans isomerization of tetragonal-planar $[PtX_2L_2]$ complexes: (A) in nonpolar solvents, (B) in nonpolar solvents in the presence of small quantities of a polar solvent S, (C) in polar solvents (*e.g.*, S = MeOH).

concentration [L] ≈ 0. Under these conditions eq 14 simplifies to (see Figure 2)

$$\text{rate} \approx \frac{k_1 k_6[L_0]^2}{[S]^2(k_1 + k_5)} = k'[L_0]^2 \qquad (15)$$

That is to say that in bulk MeOH solution the rate of trans to cis isomerization would exhibit a second-order dependence on the amount of added ligand and be independent of the concentration of platinum complex.

To test the applicability of eq 15 we have carried out uv kinetic studies of the Me_2PhP catalyzed trans to cis isomerization of $[PtI_2(Me_2PhP)_2]$ in MeOH solution at varying concentrations of added Me_2PhP. After an initial period of *ca.* 2 min, prior to steady-state conditions, pseudo-zero-order kinetic behavior was observed from which a pseudo-zero-order rate constant characteristic of a particular concentration of added Me_2PhP was obtained. A plot of the observed pseudo-zero-order rate constants *vs.* added Me_2PhP concentration to the second power ($[Me_2PhP]^2$) gives the linear correlation shown in Figure 2. Thus these kinetic data are consistent with a consecutive displacement mechanism for L catalyzed trans to cis isomerization of $[PtX_2L_2]$ as outlined in Scheme III.

The effect of solvent polarity on the L catalyzed cis–trans isomerization of $[PtX_2L_2]$ is clearly illustrated by the qualitative potential energy profiles for cis–trans isomerization shown in Figure 3.

Conclusion

The available data concerning the mechanism of the phosphine catalyzed cis–trans isomerization of tetragonal-planar complexes of platinum(II) of the type $[PtX_2(PR_3)_2]$ are fully consistent with the consecutive displacement mechanism involving an ionic intermediate (as shown in Schemes II and III) and known ligand trans effects. While the data presented to date do not disprove a pseudorotational mechanism for cis–trans isomerization, there is no clear reason for evoking such a mechanism. Indeed such a mechanism appears unlikely for platinum(II) complexes where stereochemically specific SN2 ligand substitution (*i.e.*, the trans effect) is a pronounced feature of their reactivity.

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