Public Health Service Grant No. GM-12152 from the National Institute of General Medical Sciences.

Registry No. Cu($H_{-3}G_3a$)lut$^-$, 72658-92-5; Cu($H_{-3}G_3a$)(γ-pic)$^-$, 72658-93-6; Cu($H_{-3}G_3a$)py$^-$, 72658-94-7; Cu($H_{-2}G_3$)lut$^-$, 72658-95-8; Cu($H_{-2}G_3$)py$^-$, 72658-96-9; Cu($H_{-2}G_3$)Br^{2-}, 72658-97-0; Cu($H_{-2}G_2a$)lut, 72658-98-1; Cu($H_{-2}G_2a$)py, 72658-99-2; Ni($H_{-2}G_3$)lut$^-$, 72659-00-8; Ni($H_{-2}G_2a$)lut, 72692-63-8; Ni($H_{-2}G_2a$)py, 72659-01-9; Ni($H_{-2}G_2a$)(α-pic), 72659-02-0; Ni($H_{-3}G_3a$)$^-$, 34722-97-9; Cu(aq)$^{2+}$, 14946-74-8; Co(en)$_3{}^{3+}$, 14878-41-2; trien, 112-24-3; lut, 108-48-5.

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Normal- and High-Pressure Kinetics and Mechanism of the Cis–Trans Isomerization of $PtXR(PEt_3)_2$ Complexes. Evidence for an Initial Solvolysis Step

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It has been previously postulated that the spontaneous cis–trans isomerization of $PtXR(PEt_3)_2$, where R = alkyl or aryl groups and X = halides, occurs through the three-coordinate intermediate $PtR(PEt_3)_2{}^+$, which is in a steady state during the reaction. High-pressure kinetics have now revealed a $\Delta V^\ddagger$ value of -12 cm^3 mol^{-1} for the first step in this mechanism. Therefore this step must be considered to be associative. Kinetics at atmospheric pressure show that the intermediate species is not in a steady state, but rather a preequilibrium exists. These data are consistent with an initial solvolysis step and also establish that the rate of solvolysis of *cis*-$PtXR(PEt_3)_2$ is faster than the rate of the subsequent isomerization reaction. A $\Delta V^\ddagger$ value of $+7.7$ cm^3 mol^{-1} was found for the isomerization reaction. This can be interpreted either as a dissociation of the intermediate *cis*-$PtR(MeOH)(PEt_3)_2{}^+$ or as an intramolecular rearrangement of this species.

Introduction

The catalyzed cis–trans isomerization of square-planar d^8 complexes is believed to proceed, depending on the conditions, either via pseudorotation of a five-coordinate intermediate or through a consecutive displacement of ligands.[1] The spontaneous cis–trans isomerization in polar solvents most likely follows the latter mechanism with the solvent acting as a catalyst.

Romeo et al.[2] studied the spontaneous isomerization

$$cis\text{-}PtXR(PEt_3)_2 \xrightarrow{MeOH} trans\text{-}PtXR(PEt_3)_2 \qquad (1)$$

(R = alkyl, aryl, or substituted aryl groups and X = Cl or Br), as well as various substitution reactions of these cis complexes:[2]

$$cis\text{-}PtBrR(PEt_3)_2 + Y^- \xrightarrow{MeOH} cis\text{-}PtYR(PEt_3)_2 + Br^- \qquad (2)$$

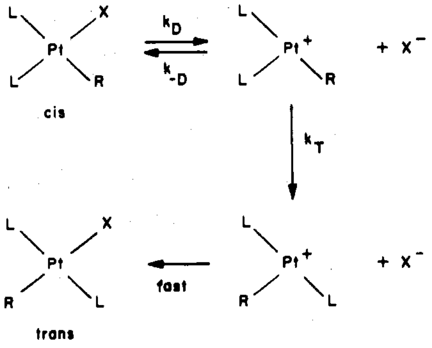
(Y = halide or pseudohalide). Surprisingly they found that, with the exception of R = mesityl, the observed isomerization rate constant for reaction 1 is much smaller than the corresponding solvolysis rate constant for reaction 2. Only in the case of R = mesityl are the rate constants equal. Furthermore, these isomerization reactions were shown[2] to have small absolute $\Delta S^\ddagger$ values, except for R = mesityl where $\Delta S^\ddagger = -92$ J K^{-1} mol^{-1}. The authors therefore postulated a dissociative mechanism for these reactions (Scheme I).

With use of the steady-state approximation, the following rate law was derived:

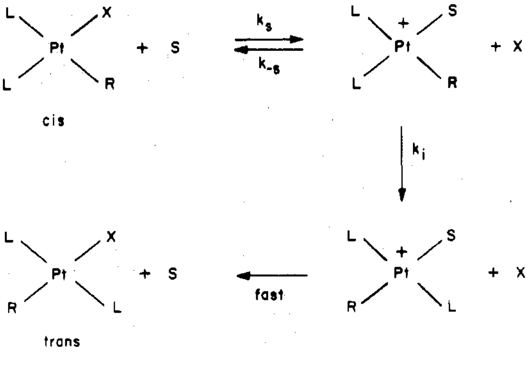
$$k_{obsd} = k_D k_T/(k_{-D}[X^-] + k_T) \qquad (3)$$

As predicted by eq 3, mass law retardation was found when halide ions were introduced into the reaction solution.[2] Since k_{obsd}(reaction 1) $\simeq k_s$(reaction 2) for R = mesityl, it was also proposed that the substitution reactions of the *cis*-PtX(mesityl)$(PEt_3)_2$ complexes follow a dissociative mechanism.

Scheme I



Scheme II



Recently an alternative explanation was proposed involving a rapid preequilibrium rather than the steady-state approximation for reaction 1 (Scheme II), leading to rate law 4.[3]

$$k_{obsd} = k_i K_s/([X^-] + K_s) \qquad (4)$$

With use of the available [Br$^-$] dependence data[2] for reaction 1, k_i and K_s were calculated.[3] As the k_s values are

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[1] Louw, W. J. *Inorg. Chem.* **1977**, *16*, 2147 and references therein.

[2] (a) Faraone, G.; Ricevuto, V.; Romeo, R.; Trozzi, M. *J. Chem. Soc. A* **1971**, 1877. (b) Romeo, R.; Miniti, D.; Trozzi, M. *Inorg. Chim. Acta* **1975**, *14*, L15. (c) Romeo, R.; Miniti, D.; Trozzi, M. *Inorg. Chem.* **1976**, *15*, 1134. (d) Romeo, R. *Ibid.* **1978**, *17*, 2040.

[3] van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 572.

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Table I. Influence of Pressure on the Observed Rate Constants for the Cis–Trans Isomerization of $PtBrR(PEt_3)_2$ in MeOH at 30 °C

R	$10^4 \times$ [added Br^-], M	μ, M	pressure, bar	$10^4 \times k_{obsd}$,[a] s^{-1}
mesityl	0	$\sim 10^{-5}$	1	1.76
			250	2.00
			500	2.19
			750	2.53
			1000	2.76
			1250	2.93
			1500	2.95
			1750	2.87
mesityl	0	0.01	1	2.01
			500	2.44
			1000	2.94
			1500	3.65
phenyl[b]	0	$\sim 10^{-5}$	1	17.2
			500	14.0
			1000	12.15
			1500	10.6
phenyl[b]	0	0.01	1	26.05
			500	21.3
			1000	17.9
			1500	15.8
phenyl	2	0.01	1	3.0
			500	2.7
			1000	2.35
			1500	2.04
phenyl	3	0.01	1	2.1
			500	1.97
			1000	1.68
			1500	1.43
phenyl	4	0.01	1	1.6
			500	1.48
			1000	1.30
			1500	1.12
phenyl	5	0.01	1	1.29
			500	1.2
			1000	1.03
			1500	0.95
phenyl	6	0.01	1	1.1
			500	1.0
			1000	0.883
			1500	0.79
phenyl	12	0.01	1	0.55

[a] Average of two or more values. In the absence of added Br^-: $k_{obsd} = k_i$ (R = phenyl); $k_{obsd} = k_s$ (R = mesityl). [b] [complex] = 1×10^{-4} M.

known from reaction 2, it could be shown that with the exception of R = mesityl, k_s, $k_{-s}[Br^-] >> k_i$ and a preequilibrium approach must be used. It was further suggested[3] that only for R = mesityl ($k_{-s}[Br^-] \simeq k_i > k_s$), should a steady-state approximation be used, according to Scheme II, yielding the rate law

$$k_{obsd} = k_i k_s/(k_{-s}[X^-] + k_i) \tag{5}$$

Since at low $[X^-]$ rate equations (4) and (5) limit to k_i and k_s, respectively, it is apparent that k_{obsd}(reaction 1) < k_s(reaction 2) for R ≠ mesityl, while $k_{obsd} \simeq k_s$ for R = mesityl. Furthermore, from the pressure dependence of k_s for R = mesityl, $\Delta V^{\neq}$ values of −14.1 and −17 $cm^3\ mol^{-1}$ were observed[3] for the respective nucleophiles I^- and $SC(NH_2)_2$, thereby substantiating the idea that the k_s path in reaction 1 is an associative solvolysis step.

We have now extended the investigation of the kinetics of reaction 1 for X = Br and R = mesityl and phenyl in methanol under normal- and high-pressure conditions. As a result of this research, we were able to distinguish between the mechanisms in Schemes I and II.

Table II. Influence of the Initial Complex Concentration on the Initial Rate of the Cis–Trans Isomerization of $PtBr(phenyl)(PEt_3)_2$ in MeOH at 30 °C and μ = 0.01 M ($LiClO_4$)[a]

$10^4 c_0$, M	$10^4 c_t$, M	$10^8 dc/dt$, $M\ s^{-1}$	$10^{-3} dt \times (c_t)/dc$, s	$10^2(K_s + 4c_t)^{1/2}$, M
0.243	0.21	2.14	0.98	1.05
0.509	0.43	3.53	1.16	1.41
0.959	0.841	6.073	1.385	1.91
1.077	1.038	6.982	1.49	2.1
1.64	1.49	8.58	1.74	2.5
1.69	1.51	9.12	1.656	2.51
3.08	2.82	12.83	2.2	3.4
3.24	2.97	13.84	2.146	3.49
3.89	3.44	14.28	2.41	3.75

[a] c_0 = initial [*cis*-$PtBr(phenyl)(PEt_3)_2$]. c_t = combined [*cis*-$PtBr(phenyl)(PEt_3)_2$] and [*cis*-$Pt(phenyl)(MeOH)(PEt_3)_2^+$] after 60 s. dc = concentration change in the first 120 s. dt = 120 s. $K_s = 2.73 \times 10^{-5}$ M (Table V).

Table III. Influence of the Initial [*cis*-$PtBr(phenyl)(PEt_3)_2$] on the Extinction Coefficient at 250 nm in MeOH at 30 °C and μ = 0.01 M ($LiClO_4$) at Zero Time

$10^4[complex]_0$, M	ϵ_{250}	$10^4[complex]_0$, M	ϵ_{250}
1.87[a]	8026	1.64	7378
3.89	7584	1.077	7324
3.24	7407	0.959	7299
3.08	7468	0.509	7073
1.69	7250	0.243	7000

[a] In 6.4×10^{-3} M in LiBr.

Experimental Section

Complexes. The complexes *cis*-$PtBr(phenyl)(PEt_3)_2$ and *cis*-$PtBr(mesityl)(PEt_3)_2$ were prepared according to literature methods and identified from microanalyses and IR spectra.[4] Methanol was dried over magnesium and subsequently distilled.

Kinetics. The isomerization reactions were followed spectrophotometrically at 250 and 260 nm for R = phenyl and mesityl (X = Br), respectively, on a Zeiss DMR 10 equipped with either a thermostated (±0.05 °C) high-pressure cell[5] or a conventional, thermostated (±0.05 °C) cell compartment. The ionic strength, μ, and the $[Br^-]$ were controlled by the addition of dried $LiClO_4$ and dried LiBr, respectively.

When good first-order kinetics were observed (i.e., when R = mesityl or when LiBr was added to the reaction solution for R = phenyl), the reactions were followed for approximately 3 half-lives and the end values, A_∞, were then calculated by iterating the half-lives until all three were equal. The rate constants obtained by this method agreed extremely well with those obtained by using the experimentally observed end value. The advantage of this method over the Guggenheim method[6] is that, when a reaction is followed for 3 or more half-lives, ln $(A_t - A_\infty)$ vs. time can be plotted over the entire time range. The k_{obsd} values found for reaction 1 at different pressures, $[Br^-]$, μ, and R are shown in Table I.

In the case of R = phenyl (and when no LiBr was added to the reaction solution) plots of ln $(A_t - A_\infty)$ vs. time for the isomerization reaction were curved for $[PtBr(phenyl)(PEt_3)_2] > 5 \times 10^{-5}$ M. Therefore, for the high-pressure experiments this reaction was carried out at an effective complex concentration[7] of 5×10^{-5} M in order to obtain linear rate plots. However, some experiments were conducted under atmospheric pressure at complex concentrations $>10^{-4}$ M. Under these conditions it was necessary to use the initial rate method to estimate the rate constants. The significance and justification for these experiments will be discussed later in the text. The relevant data are listed in Tables II and III.

As the intimate isomerization mechanism has not yet been established, the k_{obsd} values were not corrected for the compressibility of the solvent methanol. The resulting $\Delta V^{\neq}$'s are shown in Table IV. Except at pressures >1000 bar for R = mesityl, all ln (rate or

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(4) (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc. A* **1959**, 4020. (b) Basolo, F.; Chatt, J.; Gray, H. B.; Pearson, R. G.; Shaw, B. L. *Ibid.* **1961**, 2207.

(5) Fleischmann, F. K.; Conze, E. G.; Stranks, D. R.; Kelm, H. *Rev. Sci. Instrum.* **1974**, *45*, 1427.

(6) Guggenheim, E. A. *Philos. Mag.* **1926**, *1*, 538.

(7) The actual complex concentration used in preparing the reaction solution was 10^{-4} M. However, the time taken to fill the cell, seal the pressure vessel, pressurize, and thermally equilibrate amounted to 1 half-life of the reaction.

Table IV. Rate and Equilibrium Constants and Volumes of Activation for the Cis–Trans Isomerization of $PtBrR(PEt_3)_2$ in MeOH at 30 °C

μ, M	$10^3 k_i$, s^{-1}	$10^4 k_s$, s^{-1}	$10^5 K_s$, M	plot
		R = Phenyl		
0.01	2.52		2.73	$1/k_{obsd}$ vs. $[Br^-]$
0.01	2.4			$dt(c_t)/dc$ vs. $(K_s + 4c_t)^{1/2}$
0.01	2.6			ln $(A_t - A_\infty)$ vs. time, [complex] $< 10^{-4}$ M
$<10^{-5}$	1.72			ln $(A_t - A_\infty)$ vs. time, [complex] $< 10^{-4}$ M
0.01	$\Delta V^{\ddagger} = +7.7 \pm 0.3$ $cm^3 mol^{-1}$			ln k_i vs. P
$<10^{-5}$	$\Delta V^{\ddagger} = +7.9 \pm 0.6$ $cm^3 mol^{-1}$			ln k_i vs. P
0.01	$\Delta V^{\ddagger} = +9.7 \pm 0.4$ $cm^3 mol^{-1}$		$\Delta V^{\ddagger} = -4.1 \pm 0.3$ $cm^3 mol^{-1}$	$1/k_{obsd}$ vs. $[Br^-]$
		R = Mesityl		
$<10^{-6}$		1.76		ln $(A_t - A_\infty)$ vs. time
0.01		2.01		ln $(A_t - A_\infty)$ vs. time
$<10^{-6}$		$\Delta V^{\ddagger} = -12.0 \pm 0.5$ $cm^3 mol^{-1}$		ln k_s vs. P
0.01		$\Delta V^{\ddagger} = -10.0 \pm 0.3$ $cm^3 mol^{-1}$		ln k_s vs. P
0.1		$\Delta V^{\ddagger} = -14.1 \pm 0.5$ $cm^3 mol^{-1}$		ref 3
$<10^{-6}$		$\Delta V^{\ddagger} = -17.0 \pm 0.7$ $cm^3 mol^{-1}$		ref 3

Table V. Effects of Pressure on the Rate and Equilibrium Constants of the Cis–Trans Isomerization of $PtBr(phenyl)(PEt_3)_2$ in MeOH at 30 °C and $\mu = 0.01$ M

pressure, bar	$10^3 k_i$, s^{-1}	$10^5 K_s$, M
1	2.52	2.73
500	2.14	2.97
1000	1.7	3.26
1500	1.42	3.47

equilibrium constant) vs. pressure plots were linear.

Results and Discussion

With the use of the known K_s values[3] (eq 4), the $[X^-]$ can be determined from the initial complex concentrations. For R = phenyl and X = Br and at complex concentration $>5 \times 10^{-5}$ M, the initial $[Br^-]$ in methanol is >10% of the parent complex concentration. As it is known that the overall isomerization reaction goes completely to the trans product, the $[Br^-]$ will decrease as the reaction proceeds, unless K_s for the trans species is coincidentally equal to K_s for the cis adduct (K_s being the equilibrium constant for the solvolysis step). Assuming the latter is not the case, then if a rapid preequilibrium exists (Scheme I or II), at high initial complex concentration the $[Br^-]$ will decrease until $[Br^-] << K_s$(cis), with the result that k_{obsd} will also change during the reaction, as dictated by eq 4.

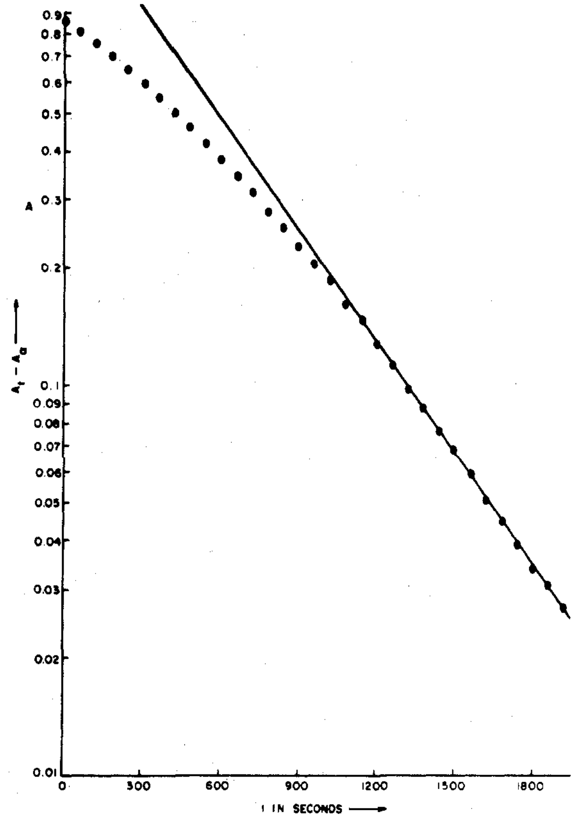

Figure 1. Graph of the logarithm of the absorbance change with time for the isomerization of *cis*-$PtBr(phenyl)(PEt_3)_2$ in methanol at 30 °C. The initial complex concentration equals 3.08×10^{-4} M.

A reinvestigation of reaction 1 for *cis*-$PtBr(phenyl)(PEt_3)_2$ at complex concentrations $>5 \times 10^{-5}$ M showed that plots of ln $(A_t - A_\infty)$ vs. time are indeed curved and limit to a straight line at concentrations $<5 \times 10^{-5}$ M, as shown in Figure 1. This phenomenon was apparently not observed previously[2] as complex concentrations of 5×10^{-5} M were employed. From the linear portion of the curve in Figure 1 a k_{obsd} value (k_i according to eq 4) of 2.6×10^{-3} s^{-1} at 30 °C and $\mu = 0.01$ M was calculated, which is about twice the previously reported value.[2] Addition of an excess of LiBr to the reaction solution caused the $[Br^-]$ term in eq 4 to remain effectively constant during the reaction, and linear plots were then observed for ln $(A_t - A_\infty)$ vs. time over the whole range of [*cis*-$PtBr(phenyl)(PEt_3)_2$]. From a plot of $1/k_{obsd}$ vs. $[Br^-]$ (from the data in Table I and application of eq 4) the k_i and K_s values could be calculated. The value for k_i of 2.52×10^{-3} s^{-1} shown in Table V compares well with the above value. Reaction 1 (R = phenyl and no LiBr added to the reaction solution) was also followed at different initial complex concentrations, c_0. From the initial part of the A_t vs. time plots, the concentration change in the first 120 s, dc, was measured, as well as the combined concentration, c_t, of the *cis*-$Pt(phenyl)(MeOH)(PEt_3)_2^+$ and *cis*-$PtBr(phenyl)(PEt_3)_2$ species after 60-s reaction time. The initial observed rate constant, $dc/[(dt)c_t]$, could then be calculated from the modified form of eq 4:

$$-dc/[(dt)c_t] = k_i k_s/([Br^-] + k_s) \qquad (6)$$

The $[Br^-]$ after 60 s was derived from c_t and K_s, which are given in Table V as 2.73×10^{-5} M, according to eq 7. On

$$[Br^-] = (-K_s + \sqrt{K_s(K_s + 4c_t)})/2 \qquad (7)$$

substitution of eq 7 into (6) and inversion, eq 8 emerges.

$$-dt(c_t)/dc = 1/2k_i + \sqrt{K_s(K_s + 4c_t)} \Big/ 2k_i K_s \qquad (8)$$

Figure 2 illustrates that a good linear relationship exists between $-dt(c_t)/dc$ and $(K_s + 4c_t)^{1/2}$. These data are given in Table II. From the intercept a k_i value of 2.4×10^{-3} s^{-1} was

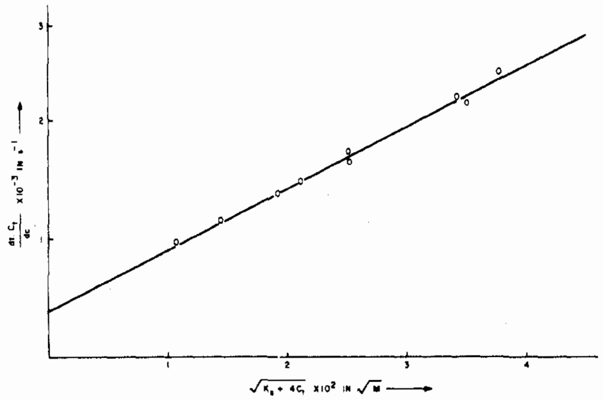

Figure 2. Dependence of the initial rate constant, $dc/[(dt)c_t]$, on [Br^-] {proportional to $(K_s + 4c_t)^{1/2}$} for the isomerization of *cis*-PtBr(phenyl)(PEt_3)$_2$ in MeOH at 30 °C.

calculated, comparing favorably with the previous two independently obtained values. Therefore it is clear that for R = phenyl and X = Br the initial concentration of *cis*-Pt(phenyl)(MeOH)(PEt_3)$_2^+$ or *cis*-Pt(phenyl)(PEt_3)$_2^+$ (and consequently the [Br^-]) is relatively high and a steady-state treatment of the respective reaction Schemes I and II is not valid, so that a preequilibrium approach must be used. This also applies to R = *o*-tolyl, *p*-tolyl, and *o*-ethylphenyl, since at high [PtBrR(PEt_3)$_2$] the [Br^-] is again >10% of the parent complex concentration. However, for R = mesityl good first-order kinetics were obtained for complex concentrations in the range (5–50) × 10^{-5} M. This result is most significant as it establishes that only for R = mesityl is the intermediate complex concentration, and therefore the [Br^-], sufficiently small that a steady-state approximation can be made.

To summarize: for R ≠ mesityl and X = Br a fast preequilibrium exists and eq 4 applies, limiting to k_i or k_T when applied to Scheme I, at low [Br^-]. Conversely, for R = mesityl and X = Br the intermediate species [*cis*-Pt(mesityl)(PEt_3)$_2$ in Scheme I or *cis*-Pt(mesityl)(MeOH)(PEt_3)$_2^+$ in Scheme II] is in a steady-state condition and rate law 5 is operative, limiting to k_s or k_D when applied to Scheme I at low [Br^-]. This explains the fact that for the most sterically restricting R group, mesityl, k_{obsd}(reaction 1) = k_s(reaction 2) whereby the corresponding $\Delta H^\ddagger$ and $\Delta S^\ddagger$ data[2] deviate so markedly from the activation parameters for the other isomerization reactions, i.e., where R = phenyl, *o*-tolyl, *p*-tolyl, and *o*-ethylphenyl.

In order to distinguish between the mechanisms described in Schemes I and II, we studied the kinetics of reaction 1 under pressure for R = mesityl and phenyl and X = Br. Figure 3 shows the relationship between ln k_s or ln k_D and pressure, *P*, for R = mesityl. The linear portion of the plot yields a $\Delta V^\ddagger$ of −12 $cm^3\ mol^{-1}$ (Table IV) which compares favorably with −14 $cm^3\ mol^{-1}$ found for the k_s path of reaction 2 where Y = I^-.[3] For Y = $SC(NH_2)_2$ the $\Delta V^\ddagger$ value[3] of −17 $cm^3\ mol^{-1}$ for the k_s path is rather inaccurate due to the small contribution of k_s to the overall rate constant (=$k_s + k_y[Y]$). It can now be seen that for *R* = mesityl and X = Br, not only are the k_s values obtained from reactions 1 and 2 comparable, but so are their $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$ values.[2,3] Therefore, the first step in the isomerization reaction involves the *associative* solvolysis of the most sterically crowded mesityl complex. Consequently, it seems only logical to suggest that the remaining isomerization reactions of the *less* sterically hindered cis isomers must also proceed via an initial associative solvolysis step. This concept conflicts with the dissociative mechanism (Scheme I) proposed originally[2] but substantiates the mechanism put forward in Scheme II.[3] The rate data of Romeo et al.[2] may therefore be treated according to rate law 4 for R ≠ mesityl and rate law 5 for R = mesityl.

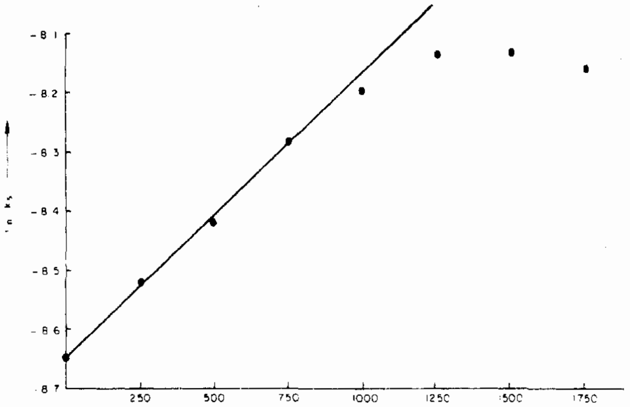

Figure 3. Influence of pressure on the solvolysis rate constant for the isomerization of *cis*-PtBr(mesityl)(PEt_3)$_2$ in MeOH at 30 °C.

The pressure dependence of k_s(reaction 1, R = mesityl and X = Br) was also measured at an ionic strength of 0.01 M ($LiClO_4$) and the $\Delta V^\ddagger$ increased slightly from −12 to −10 $cm^3\ mol^{-1}$ (Table IV). Similar secondary effects on $\Delta V^\ddagger$ have been recently observed in our laboratory for the solvolysis of Pt(dien)X^+ complexes in aqueous solution.[8] This may also explain the small differences in $\Delta V^\ddagger$ reported here and those found for the same step in the substitution reactions with I^- and thiourea[3] (Table IV).

The mechanism for the isomerization step is, however, still not clear. The pressure dependencies of the rates of reaction 1 for R = phenyl and X = Br, with and without the addition of LiBr, are given in Tables I and IV. In contrast to the acceleration of the first (solvolysis) step with increasing pressure, a deceleration was found for the second (isomerization) step. A $\Delta V^\ddagger$ of +7.7 $cm^3\ mol^{-1}$ was derived and is in keeping with the small absolute $\Delta S^\ddagger$ values recorded in the literature.[2] This strongly suggests a totally different mechanism for the isomerization step as compared to the associative solvolysis step. This finding also explains the curvature illustrated in Figure 3. As the pressure is increased, the solvolysis becomes faster while the subsequent isomerization step becomes slower, until at 1000–1500 bar, they become comparable. Scheme II consequently changes from a steady-state condition to an eventual rapid preequilibrium situation. This very unique behavior provides a substantial piece of evidence in favor of the mechanism proposed in Scheme II.

Four possible mechanisms exist for the isomerization step, viz.:

(a) A Consecutive Displacement Mechanism. This mechanism entails a series of associative reaction steps and is therefore not consistent with a positive $\Delta V^\ddagger$ of 7.7 $cm^3\ mol^{-1}$. The volumes of activation for Pt(II) solvolysis reactions, which are known to involve a purely associative mechanism, lie between −9 and −11 $cm^3\ mol^{-1}$.[8,9]

(b) A Pseudorotation of a Five-Coordinate Intermediate. The possibility that a second methanol molecule will add to *cis*-PtR(MeOH)(PEt_3)$_2^+$ to form a five-coordinate species which then pseudorotates seems rather remote. In addition, this mechanism should also yield a negative $\Delta V^\ddagger$ due to the associative entry of the second methanol molecule. Finally, if such a rotation were possible, it is difficult to rationalize why the parent *cis*-PtXR(PEt_3)$_2$ complex would also not undergo a similar rotation upon the entry of the first methanol molecule.

(c) An Equilibrium between Square-Planar and Tetrahedral Species. The calculated activation energy for this confor-

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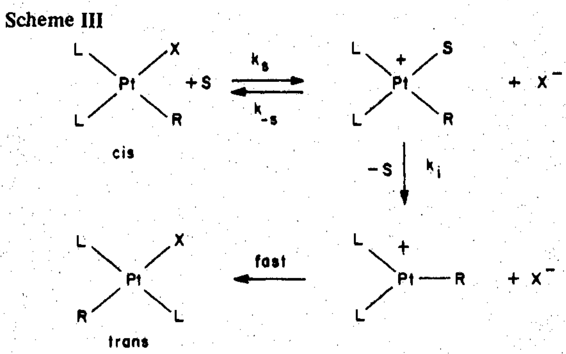
[8] Rindermann, W.; Palmer, D. A.; Kelm, H., *Inorg. Chim. Acta*, in press.

[9] Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1976**, *19*, 117.

Scheme III



mational change was found to be very high for Pt(II) and Pd(II) complexes.[10] Calculations have also shown that this cis–trans isomerization mechanism is symmetry forbidden for MX_2L_2 complexes.[11] However, the square-planar configuration of *cis*-$PtXR(PEt_3)_2$ may be so distorted as a result of steric strain that these calculations are no longer applicable. Although here again, it is rather difficult to understand why the parent complex would not also be capable of undergoing the transition to a tetrahedral conformation. Furthermore, for R = phenyl steric strain is not so acute, and yet from the activation parameters the mechanism for isomerization appears to be the same as for R = mesityl. It is difficult to predict either the sign or the magnitude of ΔV^* for such a process.

As the k_i values are of the order of 10^{-3} s^{-1} the most severe criticism of this mechanism is that conformational reactions are generally in the milli- and microsecond time range. If the k_i step is indeed in this time range, the rate-determining step must then be the uptake of Br^- by *trans*-PtR(methanol)-$(PEt_3)_2^+$ to form the trans product. However, the latter is known to be an associative process and does not therefore comply with a ΔV^* value of +7.7 cm^3 mol^{-1}. Moreover, if this were true, the substitution reaction 2 must yield mixed cis–trans products, and the solvolysis reaction must be faster than the subsequent Br^- uptake, both of which are not the case. It must therefore be accepted that the k_i path is the rate-determining step.

(d) A Dissociative Mechanism. This mechanism is probably the most likely since it can best explain the ΔV^* value of +7.7 cm^3 mol^{-1}. In Scheme III the transition state of the isomerization step is visualized as having a trigonal-planar configuration which can rapidly take up a halide ion to form the trans product. The relative weakness of the $Pt-HOCH_3$ bond may allow the normally energetically unfavorable three-coordinate transition state to compete with the five-coordinate "solvolysis" transition state.

Since a three-coordinate d^8 high-spin complex has not yet been isolated or detected as a reaction intermediate and because its existence violates Tolman's 16–18 electron rule,[12] more work needs to be done to clearly establish that isomerization results from the dissociative release of a methanol molecule from the *cis*-$PtR(MeOH)(PEt_3)_2^+$ intermediate.

It is of interest to note that for the isomerization reaction

$$\textit{trans}\text{-}PtCl_2L_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \textit{cis}\text{-}PtCl_2L_2$$

in $CDCl_3$, where L = Et_2SO and *n*-Pr_2SO,[13] a two-step process was postulated. This NMR kinetic study leads the authors[13] to propose reaction schemes similar to Schemes II and III.

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Registry No. *cis*-PtBr(phenyl)$(PEt_3)_2$, 15702-94-0; *cis*-PtBr(mesityl)$(PEt_3)_2$, 22289-37-8.

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Interaction of Copper(II) and Nickel(II) with L-Histidine and Glycylglycyl-L-histidine as an Albumin Model

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The ternary system composed of Cu(II) (M), L-histidine (A), and glycylglycyl-L-histidine (B) designed to mimic the copper-transport site of serum albumin has been investigated by potentiometric titrations and spectroscopic measurements. A solution equilibrium study (25 °C; $I = 0.1$ (KNO_3)) indicated that the binary species $CuH_{-2}B$ and CuA_2 are the main species while the ternary species CuAB is the minor one at physiological pH, and $CuH_{-2}B$ is predominant in the higher pH region. This result coincides well with the absorption, CD, and ESR spectral behaviors of the ternary systems. The quite similar absorption and CD spectral behaviors were observed for the corresponding systems with Ni(II) in place of Cu(II). In order to shed light on details of the interaction of Cu(II) with B and A, we similarly investigated the ternary systems containing histamine or glycine in place of A. The biological copper transport mechanism in blood was discussed on the basis of both the above results and the information obtained by studies on exchange reactions of Cu(II) and Ni(II) complexes of B with A, histamine and glycine.

It has been considered that the albumin-bound fraction of serum copper is in a rapid equilibrium with copper in tissues through some specific amino acid complexes and in the intermediate stage copper is bound by albumin and an amino