in a manner that is more consistent with all of the new observed structural data.

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Registry No. $Cd_3[Co(CN)_6]_2 \cdot 12H_2O$, 23540-99-0; $Cd_3[Co(CN)_6]_2$, 25359-19-7; $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$, 63976-80-7; $Mn_3[Co(CN)_6]_2$, 25868-32-0; $Fe_3[Co(CN)_6]_2 \cdot 12H_2O$, 71903-70-3; $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$, 69207-66-5; $Co_3[Co(CN)_6]_2 \cdot 12H_2O$, 26249-57-0; $Co_3[Co(CN)_6]_2$, 14123-08-1.

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Uncatalyzed Cis to Trans Isomerization of $PtX(C_6H_5)(PEt_3)_2$ Complexes in Methanol. Further Evidence for an Initial Solvolysis Step

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Kinetic data for the uncatalyzed cis to trans isomerization reactions of $PtX(C_6H_5)(PEt_3)_2$ (X = Cl, Br, I) in methanol are reported as a function of the added X^- concentration. The suggested reaction mechanism consists of a rapid preequilibration, during which the solvent-containing intermediate species *cis*-$PtS(C_6H_5)(PEt_3)_2$ is formed, followed by a rate-determining isomerization step. The rate constant for the latter reaction was found to be independent of X with an activation volume of 6.4 ± 0.4, 5.2 ± 0.3, and 7.2 ± 0.8 $cm^3\ mol^{-1}$ for X = Cl, Br, and I, respectively, at 30 °C and an ionic strength of 0.01 M. In addition, conductometric data for the preequilibrium step and kinetic data for the substitution reactions of *cis*-$PtX(C_6H_5)(PEt_3)_2$ are reported as further evidence for the suggested mechanism.

Introduction

A dissociative mechanism (Scheme I) has been postulated[3] for isomerization reaction 1, where X = halide and R = alkyl, aryl, or substituted aryl. The rate law for the suggested mechanism was derived[3] by applying the steady-state approximation to the *cis*-$PtR(PEt_3)_2$ species and is represented by eq 2.

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

$$k_{\text{obsd}} = \frac{k_D k_T}{k_{-D}[X^-] + k_T} \approx k_D \quad (\text{at low } [X^-]) \qquad (2)$$

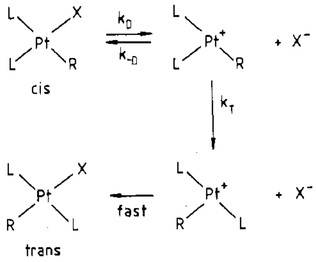
It was recently proposed[4] that an associative mechanism (Scheme II) should rather be used to explain reaction 1, in which the *cis*-$PtXR(PEt_3)_2$ species are present in a fast preequilibrium with the respective *cis*-$PtSR(PEt_3)_2$ species. Under such conditions rate law 3 is applicable. In this mechanism k_i is the rate-determining step and explains why the isomerization reaction is slower than the solvolysis reaction. It was further proposed[4] that only for the most bulky R group (when the isomerization and solvolysis rates are the same) should a steady state approximation be used, resulting eq 4 such that k_s is now the rate-determining step.

$$k_{\text{obsd}} = \frac{k_i K_s}{[X^-] + K_s} \approx k_i \quad (\text{at low } [X^-]) \qquad (3)$$

$$k_{\text{obsd}} = \frac{k_i k_s}{k_{-s}[X^-] + k_i} \approx k_s \quad (\text{at low } [X^-]) \qquad (4)$$

The following evidence in favor of Scheme II (rate laws 3 and 4) has been reported.

Scheme I



(a) For X = Br and R = Mesityl (Rate Law 4). (i) the isomerization rate constant (in the absence of added Br^-, i.e., $k_{\text{obsd}} \approx k_s$), $\Delta H^‡$, $\Delta S^‡$, and $\Delta V^{‡}$[3–5] agree within experimental error with the relevant parameters found for the solvolysis[3,4] of *cis*-PtBr(mesityl)$(PEt_3)_2$. (ii) $\Delta V^‡$ values[4,5] of −14 ± 2 $cm^3\ mol^{-1}$ and $\Delta S^‡$ values[3,4] of −18 ± 4 cal $K^{-1}\ mol^{-1}$ are consistent with an associative step.

(b) For X = Br and R = Phenyl (Rate Law 3). (i) Semilog plots of optical density change vs. time for reaction 1 deviate from linearity[5] at [complex] > 5 × 10^{-5} M. This is in agreement with a fast preequilibrium step (Scheme II), causing the initial $[Br^-]$ to be comparable with the K_s value and, therefore, resulting in a slower initial rate. As the bromide ions are incorporated into the trans product, the $[Br^-]$ decreases to a point where $[Br^-] \ll K_s$ such that linearity is obtained in the semilog plots.[5] On the addition of Br^- to the reaction solution, the $[Br^-]$ term in rate law 3 becomes constant and no curvature is observed.[5] (ii) From the linear plot of dtc_t/dc vs. $(K_s + 4c_t)^{1/2}$ (dc/dt = initial rate, c_t = initial complex concentration), the k_i value (rate law 3) obtained from the intercept[5] agreed within experimental error limits with those measured independently.[5]

A further crucial experiment in order to distinguish between the mechanisms outlined in Schemes I and II would be to study the influence of different X ligands on the magnitude of the observed isomerization rate constant. k_i (Scheme II, rate law 3) should be independent of the nature of X, whereas large variations are expected for the corresponding k_D or k_s values (Scheme I, rate law 2, or Scheme II, rate law 4). The results of such an investigation are reported in this paper.

Experimental Section

Materials. Methanol was distilled over magnesium. All other chemicals were of analytical reagent grade and dried in vacuo. *cis*-$PtX(C_6H_5)(PEt_3)_2$ (X = Cl, Br) were prepared according to

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Scheme II

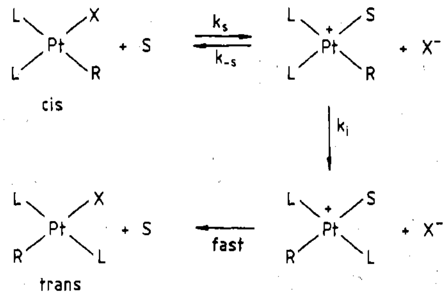

Table I. Observed Rate Constants for the Cis to Trans Isomerization of PtX(C$_6$H$_5$)(PEt$_3$)$_2$ in Methanol[a]

X	10^4[Pt], M	wavelength, nm	10^4[X$^-$], M	10^3k_{obsd},[b] s^{-1}
Cl	1.8	250	0	2.10
			4	1.33
			8	0.85
			12	0.71
			16	0.57
			20	0.50
Br	1.7	250	0	2.55
			4	0.77
			8	0.44
			12	0.34
			16	0.21
I	1.6	258	0	1.38
			1.58	0.20
			3.16	0.13
			4.74	0.083
			6.32	0.058

[a] Ionic strength = 0.01 M (LiClO$_4$), temperature = 40 °C. [b] Average value of between two and four kinetic runs.

literature methods.[6] X = I, SCN, and CN complexes were prepared by metathetical exchange with NaX in acetone. Microanalyses were in good agreement with the theoretically expected values.

Kinetics. The isomerization reactions were studied spectrophotometrically in the thermostated (±0.1 °C) cell compartments of a Unicam SP 1800 and a Cary 15 spectrophotometer. The substitution reactions were studied on a Durrum D 110 stopped-flow spectrophotometer. First-order rate constants were calculated in the usual way. High-pressure kinetic measurements were performed on a Zeiss PMQ II spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell.[7]

Results and Discussion

While this work was in progress, Romeo and co-workers[8] reported kinetic data for the isomerization of *cis*-PtX(C$_6$H$_5$)(PEt$_3$)$_2$ (X = Cl, Br, I) as a function of the concentration of X$^-$ in solution. By plotting k_{obsd}^{-1} vs. [X$^-$], they[8] find that the intercept, i.e., k_i, k_D, or k_s, does change with different X (see Figure 1 of ref 8). However, we have pointed out[9] that this figure is rather misleading since it only includes data over a limited [X$^-$] range. We have, therefore, replotted their[8] data and included all the experimental points, from which it follows that the intercepts for various X are indeed very close. This is also seen in the values k_i^{-1} (intercept), summarized in Table II, which were obtained through a least-square fit of the data reported by Romeo and co-workers.[8]

We measured these isomerization reactions at 40 °C (Table I) and estimated the rate parameters in the way outlined above (Table II). Our values of k_i^{-1} (and k_i) clearly illustrate that the intercepts are indeed constant within the experimental error limits, from which we conclude that these data further substantiate the validity of rate law 3 (Scheme II) and disprove the mechanism in Scheme I. The values of K_s in Table II are as expected and decrease significantly in the series X = Cl > Br > I.

Table II. Rate, Equilibrium, and Activation Parameters for the Cis to Trans Isomerization of PtX(C$_6$H$_5$)(PEt$_3$)$_2$ in Methanol[a]

	X		
	Cl	Br	I
$10^{-2}k_i^{-1}$, s[b]	1.84 ± 0.16	7.01 ± 0.85	16.3 ± 10.2
$10^{-6}(k_iK_s)^{-1}$, M^{-1} s	4.42 ± 0.02	10.0 ± 0.1	183 ± 6
10^3k_i, s^{-1}	5.4 ± 0.5	1.4 ± 0.2	0.6 ± 0.4
10^5K_s, M	4.2 ± 0.4	7.0 ± 0.9	0.9 ± 0.6
$10^{-2}k_i^{-1}$, s[c]	4.85 ± 0.34	2.56 ± 2.57	5.25 ± 5.82
$10^{-6}(k_iK_s)^{-1}$, M^{-1} s	0.78 ± 0.03	2.59 ± 0.26	25.4 ± 1.5
10^3k_i, s^{-1}	2.1 ± 0.1	3.9 ± 3.9	1.9 ± 2.1
10^5K_s, M	62 ± 7	10 ± 11	2.1 ± 2.4
$\Delta H_i^{\ddagger}$, kcal mol^{-1}	26.7 ± 0.6	*d*	*d*
$\Delta S_i^{\ddagger}$, cal K^{-1} mol^{-1}	+14.5 ± 1.8		
$\Delta V_i^{\ddagger}$,[e] cm^3 mol^{-1}	6.4 ± 0.4	5.2 ± 0.3	7.2 ± 0.8

[a] Ionic strength = 0.01 M (LiClO$_4$). [b] Values estimated from data at 30 °C in Table III of ref 8 (see ref 9). [c] Values estimated from data at 40 °C in Table I. [d] See Discussion. [e] Measured at 30 °C (this study).

The large errors in the k_i values originate from the initial curvature in the semilog plots of optical density change vs. time. This effect has been treated in detail before[5] and is more marked at low [X$^-$] or in absence of added X$^-$. It is not clear why this phenomenon was not previously observed and/or reported by other investigators.[8] For X = SCN, linearity in the semilog plots was only obtained in the presence of added SCN$^-$, under which conditions the reaction became so slow that no meaningful intercept could be calculated from the k_{obsd}^{-1} vs. [SCN$^-$] plot.

The degree of curvature in the semilog plots increases along the series X = Cl < Br < I < SCN and with increase in temperature. Meaningful activation parameters could, therefore, only be obtained for X = Cl (measured in the absence of added X$^-$, i.e., $k_{obsd} = k_i$) and their values are reported in Table II. Furthermore, the observed curvature lessens at higher pressures which made it possible to estimate $\Delta V_i^{\ddagger}$ from the pressure dependence of k_{obsd} ($=k_i$) in the absence of added X$^-$. The value of $\Delta V_i^{\ddagger}$ (see Table II) is, within experimental error range, independent of X and is, therefore, in agreement with our suggested mechanism outlined in Scheme II. For the alternative mechanism (Scheme I) one would expect $\Delta V^{\ddagger}$ to depend on the nature and size of X. Our value of 5.2 ± 0.3 cm^3 mol^{-1} for X = Br is in agreement with that reported earlier.[5] The magnitude of $\Delta S^{\ddagger}$ (X = Cl) and the average value of 6.3 ± 1.0 cm^3 mol^{-1} for $\Delta V_i^{\ddagger}$ (various X) may favor a dissociative mechanism for the isomerization reaction of the solvento species (*cis*-PtSR(PEt$_3$)$_2^+$). However, pseudorotation of some sort of five-coordinate species followed by a rate-determining dissociation step to yield the four-coordinate trans product cannot be ruled out as a possible mechanism.

In addition to the above outlined arguments, we have tried to measure the magnitude of the preequilibrium constant K_s (Scheme II) according to a nonkinetic method, viz., conductometrically. We have adopted equation 5, which was developed to measure the dissociation constant of a weak acid,[10] for this purpose.

$$c\Lambda = -K\Lambda_\infty + \frac{K\Lambda_\infty^2}{\Lambda} \qquad (5)$$

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(6) (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.

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(8) Romeo, R.; Minitti, D.; Lanza, S. *Inorg. Chem.* **1979**, *18*, 2362.

(9) van Eldik, R.; Palmer, D. A.; Kelm, H.; Louw, W. J. *Inorg. Chem.*, in press.

(10) Moelwyn-Hughes, E. A. "Physikalische Chemie"; Georg Thieme Verlag: Stuttgart, 1970; p 465.

Table III. Rate Constants for the Reactions *cis*-$PtX(C_6H_5)(PEt_3)_2 + Y^- \rightarrow$ *cis*-$PtY(C_6H_5)(PEt_3)_2 + X^-$ in Methanol[a]

X	Y	10^4[Pt], M	10^3[added X^-], M	[Y^-], M	k_{obsd},[b] s^{-1}	k_s, s^{-1}	k_y, M^{-1} s^{-1}
Cl	Br	2.39	1.18	0.05	3.30	2.94 ± 0.01	7.25 ± 0.14
				0.03	3.15		
				0.01	3.01		
	I	2.50	1.58	0.051	3.62	2.91 ± 0.03	13.2 ± 0.8
				0.041	3.43		
				0.031	3.30		
				0.020	3.14		
				0.010	3.07		
				0.005	2.99		
			7.50	0.051	3.65		
				0.041	3.56		
	SCN	2.35	0.69	0.05	31.0	1.8 ± 0.6	587 ± 20
				0.02	14.1		
				0.005	4.42		
Br	I	2.10	0.90	0.05	5.23	4.61 ± 0.02	11.9 ± 0.8
				0.04	5.07		
				0.03	4.92		
				0.02	4.85		
				0.01	4.75		
				0.005	4.66		
I	SCN	1.90	2.34	0.05	34.7	0.61 ± 0.35	678 ± 12
				0.04	27.8		
				0.02	13.5		
				0.005	3.93		
				0.0025	2.77		
			0.47	0.05	35.1		
SCN	CN	1.70	0.50	0.025	56.6	−1.7 ± 0.8	2367 ± 52
				0.020	47.3		
				0.015	33.2		
				0.010	21.7		
				0.005	9.90		
				0.0025	4.48		

[a] Temperature = 30 °C. [b] Average value of up to eight kinetic runs.

The molar conductance Λ was measured as function of complex concentration c, immediately after the complex had been dissolved in methanol at 25 °C. All conductivity measurements were corrected for the contribution of the solvent, and the value of K (i.e., K_s in this study) was obtained from the slope and the intercept of a plot of $c\Lambda$ vs. $1/\Lambda$. In this method no assumption as to the magnitude of Λ_∞ had to be made, which is an advance over the method adopted by Romeo and co-workers.[8] K_s turned out to be 5.6×10^{-5}, 13×10^{-5}, and 1.0×10^{-5} M^{-1} for X = Cl, Br, and I, respectively, which are indeed very close to those reported for K_s at 30 °C in Table II. Although it is generally accepted that such measurements in nonaqueous solvents are not very accurate, the magnitude of the above values are such that they surely underline the validity of our proposed mechanism (Scheme II).

In agreement with Scheme II and rate law 3, k_s should be larger than k_i. Accordingly, k_{obsd} was measured for the substitution reactions

$$cis\text{-}PtX(C_6H_5)(PEt_3)_2 + Y^- \rightarrow cis\text{-}PtY(C_6H_5)(PEt_3)_2 + X^-$$

X = Cl; Y = Br, I, SCN
X = Br; Y = I
X = I; Y = SCN
X = SCN; Y = CN

for which the data are summarized in Table III. Such substitution reactions proceed by the well-known[11] two-term rate law

$$k_{obsd} = k_s + k_y[Y]$$

in which k_y is the rate constant for the direct attack of Y^-. Free X^- was added to the reaction mixtures in order to prevent the isomerization reactions, and k_{obsd} was found to be independent of [X^-] over the concentration ranges concerned. The values of k_s and k_y were calculated from a least-square fit of the k_{obsd} vs. [Y] data and are included in Table III. It follows that k_s is significantly larger than k_i (Table II), in agreement with our preequilibrium postulation. No meaningful k_s value for X = SCN could be obtained, due to the dominating k_y value.

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Registry No. *cis*-$PtCl(C_6H_5)(PEt_3)_2$, 15702-92-8; *cis*-$PtBr(C_6H_5)(PEt_3)_2$, 15702-94-0; *cis*-$PtI(C_6H_5)(PEt_3)_2$, 56553-44-7; *cis*-$Pt(SCN)(C_6H_5)(PEt_3)_2$, 74231-19-9; *cis*-$Pt(MeOH)(C_6H_5)(PEt_3)_2^+$, 74280-92-5; Br^-, 24959-67-9; I^-, 20461-54-5; SCN^-, 302-04-5; CN^-, 57-12-5.

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