

Contribution from the Institute for Physical Chemistry,
University of Frankfurt, 6 Frankfurt am Main, West Germany

Substitution Reactions of *cis*- and *trans*-Bis(triethylphosphine)mesityl(bromo)platinum(II) with Iodide and Thiourea in Methanol. Evidence for an Associative Mechanism¹

R. VAN ELDIK,² D. A. PALMER, and H. KELM*³

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The pressure and temperature dependencies of the rates of substitution of *cis*- and *trans*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] by iodide and thiourea have been studied in methanol. The volumes of activation are all negative, between -11 and -16 cm³ mol⁻¹, for both the nucleophile independent (*k*₁) and dependent (*k*₂) paths. Values for Δ*H*[‡] and Δ*S*[‡] for the *cis* to *trans* isomerization process are also reported. The results are discussed with reference to recent literature data and are interpreted in terms of associative processes.

Introduction

There has been a growing interest in the substitution reactions of sterically hindered square-planar complexes over the past few years. This is mainly due to a search for ways in which the normal mode of substitution in these complexes, namely via an associative mechanism,⁴ can be influenced with the ultimate conversion of the process to a dissociative mechanism. Massive steric hindrance is thought to be a way of stabilizing a three-coordinate d⁸ state, thereby favoring a dissociative mechanism.⁴⁻⁶

Substitution reactions of [Pd(dien)Cl]⁺ are ~10⁵ times faster than the corresponding reactions of [Pd(Et₄dien)Cl]⁺ and [Pd(MeEt₄dien)Cl]⁺^{4,7,8} where Et₄dien = 1,1,7,7-tetraethyldiethylenetriamine and MeEt₄dien = 4-methyl-1,1,7,7-tetraethyldiethylenetriamine. It was suggested that steric hindrance prevented bimolecular associative attack such that the previously less favorable dissociative mechanism became significant. For a series of nucleophiles, the nucleophile-dependent term in the usual two-term rate law was reported^{7,8} to disappear for the substitution reactions of N-substituted dien complexes, although later work⁹ indeed showed that this term had merely become small under the experimental conditions used. Furthermore, aprotic solvents seem to assist the dissociative path of such sterically hindered substitution processes.⁸ In addition, steric crowding in these complexes manifests itself in linkage isomerization of the normally stable S-bonded thiocyanate and Se-bonded selenocyanate.^{10,11}

A similar situation was reported¹² for the corresponding reactions of Au(III) complexes, where the nucleophile-dependent path disappeared on going from dien to Et₄dien complexes, and a solvent-assisted dissociation process was suggested. Little information is available for the analogous Pt(II) systems,⁶ since the sterically hindered reactions become extremely slow. Nevertheless, a dissociative mechanism was proposed. The photosubstitution reactions of such N-substituted dien-Pt(II) complexes have been studied in more detail.^{13,14}

Another source of steric hindrance is found^{4,6} in *cis*- and *trans*-[Pt(PEt₃)₂RX] complexes, where R is an alkyl or aryl group and X a halide atom. The initial investigation¹⁵ of the reactions of such complexes with pyridine in ethanol showed a decrease in the reaction rate for various R substituents in the order phenyl, *o*-tolyl, mesityl, the effect being much more prominent for the *cis* than for the *trans* complexes. The results were discussed in terms of a displacement process involving a trigonal-bipyramidal intermediate, i.e., an associative type mechanism. In later work^{16,17} it was shown that the *trans* complexes do not undergo direct bimolecular attack during this reaction and that the intermediate, *trans*-[Pt(PEt₃)₂R-(MeOH)]⁺, plays an important role. The *cis* complexes undergo spontaneous isomerization to the *trans* form before or during their reaction with pyridine.^{16,17} The influence of

the entering group on the *trans* effect of the R group and the solvent effect on the leaving group were investigated¹⁸⁻²² for substitution reactions of complexes of the type *trans*-[Pt(PEt₃)₂RX], where R = CH₃, C₆H₅, *m*-MeC₆H₄, *o*-MeC₆H₄, and 2,4,6-Me₃C₆H₂. The associative character of such reactions and the importance of solvational changes in the transition state²² were emphasized.

Romeo and co-workers²³⁻²⁵ recently reported data for the *cis* to *trans* isomerization and methanol solvolysis of *cis*-[Pt(PEt₃)₂RX] (R = C₆H₅, *p*-MeC₆H₄, *o*-MeC₆H₄, *o*-EtC₆H₄, 2,4,6-Me₃C₆H₂; X = Cl, Br). They conclude that isomerization proceeds via a dissociative asynchronous mechanism in which the rate-determining step is Pt-Br bond cleavage to yield a three-coordinated "cis-like" intermediate. However, solvolysis proceeds via an associative mode of activation for the unhindered complexes and via a dissociative mechanism for the sterically crowded complex *cis*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br].

The volume of activation Δ*V*[‡]_{exp}, derived from the pressure dependence of the rate constant of a reaction, has been used with success²⁶⁻²⁸ as a criterion to distinguish between associative and dissociative reaction paths. In an effort to establish the intimate mechanism involved in the reactions of such sterically crowded complexes, we have chosen to study the pressure and temperature dependencies of the reactions of *cis*- and *trans*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] with iodide and thiourea in methanol.

Experimental Section

The complexes *cis*- and *trans*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] were synthesized from *cis*-[Pt(PEt₃)₂Cl₂]²⁹ according to standard procedures.^{15,30} Their composition was substantiated by chemical analysis³⁷ and by a comparison of their melting points and IR spectra (Beckman IR 4240 using KBr disks) with the corresponding data in the literature.^{15,25,30} Methanol was dried over Mg and subsequently distilled. All other materials used were of analytical grade.

The isomerization of *cis*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] was followed spectrophotometrically in the thermostatted (±0.05 °C) cell compartment of a Zeiss PMQ II spectrophotometer. The changes in absorbance were too small to allow in situ kinetic measurements to be performed under pressure. The reactions of *cis*- and *trans*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] with iodide were studied in the same spectrophotometer and in a Zeiss DMR 10, equipped with a thermostatted (±0.05 °C) high-pressure cell.³² The reactions with thiourea were followed conductometrically in a thermostatted (±0.05 °C) high-pressure conductivity cell,³³ using a Wayne Kerr B 642 Autobalance Bridge. Stock solutions of both complexes were stored at -20 °C to inhibit isomerization and/or solvolysis.

The observed first-order rate constants *k*_{obsd} were calculated from the slopes of ln (*F*_{*t*} - *F*_∞) vs. time plots, where *F*_{*t*} and *F*_∞ are the absorbances or conductivities at time *t* and at infinity, respectively. These plots were linear for at least 2 to 3 half-lives. A large excess of nucleophile was always used in the substitution reactions to ensure pseudo-first-order conditions. No attempt was made to correct the *k*_{obsd} values of the compressibility of the solvent. The activation

Table I. Temperature Dependence of k_{obsd} for the Isomerization of *cis*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] in Methanol^{a,b}

temp, °C	$k_{\text{obsd}} \times 10^4, \text{s}^{-1}$	temp, °C	$k_{\text{obsd}} \times 10^4, \text{s}^{-1}$
17.0	0.462	36.2	4.18
	0.444		3.34
23.5	0.899		4.20
	0.946	44.6	9.11
	1.00		9.14
30.0	2.07		10.0
	1.89		
	1.75		

^a [Pt(II)] = 5×10^{-4} M, wavelength 290 nm. ^b $\Delta H^\ddagger = 81.9 \pm 1.6$ kJ mol⁻¹ and $\Delta S^\ddagger = -45.2 \pm 5.5$ J K⁻¹ mol⁻¹.

Table II. Temperature and Pressure Dependence of k_{obsd} for the Reaction *cis*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] + I⁻ in Methanol^a

temp, °C	pressure, bar	$k_{\text{obsd}} \times 10^4, \text{s}^{-1}$	activation parameters
17.0 ^b	1	0.572	$\Delta H^\ddagger = 75.9 \pm 0.6$ kJ mol ⁻¹
		0.573	
		0.538	
23.5 ^b	1	1.06	
		1.11	
34.8 ^b	1	3.61	$\Delta S^\ddagger = -64.0 \pm 1.9$ J K ⁻¹ mol ⁻¹
		3.63	
43.6 ^b	1	8.46	
		8.63	
30.0	1	1.92 ^c	
		1.82 ^c	
		1.89	
	10	2.26	
		2.26	
		2.29	
		2.35	
	250	2.65	
		2.65	
		2.54	
		2.50	
	500	3.21	$\Delta V^\ddagger_{\text{exp}} = -14.1 \pm 0.5$ cm ³ mol ⁻¹
		3.11	
		3.03	
	750	3.66	
		3.60	
		3.34	
		3.31	
	1000	3.96	
		4.33	
		3.86	
		4.36	
	1250	4.14	
		4.77	
		4.84	
		4.29	
	1500	6.01	
		5.37	
		5.21	
		5.16	

^a [Pt(II)] = 2.5×10^{-4} M, [I⁻] = 2.5×10^{-2} M, wavelength 300 nm. ^b [Pt(II)] = 5×10^{-4} M. ^c [I⁻] = 1×10^{-2} M.

parameters (ΔH^\ddagger , ΔS^\ddagger , and $\Delta V^\ddagger_{\text{exp}}$) were calculated in the usual way. All plots of $\ln k_{\text{obsd}}$ vs. pressure were linear, within experimental error, over the pressure ranges concerned.

Results

The isomerization reaction was found to virtually go to completion, whereas the substitution reactions studied go to completion with retention of configuration.²⁵ Rate data for the isomerization of *cis*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] as a function of temperature are summarized in Table I.

Table II contains the rate data for the reaction of *cis*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] with iodide as a function of temperature and pressure. The observed first-order rate constants are independent of [I⁻] as illustrated by the data at normal pressure and 30 °C. A noteworthy result is the increase in k_{obsd} from $(1.86 \pm 0.05) \times 10^{-4}$ to $(2.29 \pm 0.04) \times 10^{-4}$ s⁻¹ over the pressure range 1–10 bar. The plot of $\ln k_{\text{obsd}}$ vs. pressure is linear over the 10–1500 bar pressure range, and the value of k_{obsd} at normal pressure does not fit into this plot. It was established that this inconsistency is not the result of contamination of the methanol solution by the pressurizing medium. We cannot offer any reasonable explanation for this phenomenon and must ascribe it to some physical deviation in the system or measuring procedure. Due to this abnormality, the values of k_{obsd} at normal pressure and 30 °C were not included in the calculations of the activation parameters quoted in Table II.

Table III. Temperature and Pressure Dependence of k_{obsd} for the Reaction *trans*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] + I⁻ in Methanol^a

temp, °C	pressure, bar	$k_{\text{obsd}} \times 10^4, \text{s}^{-1}$			$k_1 \times 10^4, \text{s}^{-1}$	$k_2 \times 10^4, \text{M}^{-1} \text{s}^{-1}$
		[I ⁻], M				
		0.01	0.05	0.10		
23.8	10	1.07	1.16	1.24	1.06	1.93
36.0	10	4.21	4.32	4.68	4.12	5.29
44.7	10	9.37	9.88	10.4	9.28	11.1
50.0	10	16.4	16.1	16.0	16.2	
30.0	10	2.21	2.40	2.60	2.14	4.59
		2.12	2.41	2.57		
	250	2.56	2.85	3.24	2.43	8.43
		2.50	2.83	3.33		
	500	3.22	3.49	3.49	2.96	5.63
		2.68	3.24	3.46		
	750	3.55	3.84	4.29	3.54	5.67
		3.48	4.07	3.80		
	1000	4.33	4.27	5.73	4.08	10.4
		4.22	4.59	4.66		
	1250	4.76	5.20	6.27	4.80	14.8
		5.25	5.69	6.40		
	1500	5.64	5.86	7.00	5.41	11.9
		5.39	6.17	6.17		
		for k_1		for k_2		
		$\Delta H^\ddagger, \text{kJ mol}^{-1}$		79.6 ± 1.1		
		$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$		-52.3 ± 3.5		
		$\Delta V^\ddagger_{\text{exp}}, \text{cm}^3 \text{mol}^{-1}$		-15.8 ± 0.4		
				-16.4 ± 5.4		

^a [Pt(II)] = 5×10^{-4} M, ionic strength = 0.1 M (LiClO₄), wavelength 300 nm.

The rate data for the reaction of the *trans* isomer with iodide, summarized in Table III, indicate an [I⁻] dependence of k_{obsd} according to the well-known two-term rate law $k_{\text{obsd}} = k_1 + k_2[\text{I}^-]$. The contribution of the k_2 term toward k_{obsd} is rather small for this particular reaction, such that k_2 cannot be determined very accurately. This is reflected in the error limits of the reported activation parameters.

A similar two-term rate law behavior was found for the substitution reactions of the *cis* (Table IV) and *trans* isomers (Table V) with thiourea. Here the contribution of the k_2 term is more significant, and k_2 can be determined accurately. In fact, for the reaction of the *trans* isomer with thiourea (Table V) the contribution of the k_2 term becomes so large that the values of k_1 are now subjected to considerable errors. For this reason we have included the error limits of k_1 and k_2 in Table V as they provide an explanation for the large error limits in the values of the activation parameters of k_1 . In an effort to find a more accurate value for $\Delta V^\ddagger_{\text{exp}}$ for k_1 , an alternative way of treating the data was explored. At each thiourea concentration the best linear fit for $\ln k_{\text{obsd}}$ vs. pressure was obtained, from which values of k_{obsd} for the different pressures were calculated. From plots of $k_{\text{obsd}}^{\text{calcd}}$ vs. SC(NH₂)₂ new values for k_1 and k_2 could be estimated. The error limits of these values are indeed much smaller for k_1 than those reported in Table V, resulting in more accurate $\Delta V^\ddagger_{\text{exp}}$ values, as can be seen in Table VI. It must be emphasized that the above "artificial" treatment of the experimental data was only employed, as k_1 in this particular reaction is small compared to k_{obsd} and is therefore subjected to considerable errors.

The rate and activation parameters for the investigated reactions are summarized in Table VI, together with the available literature data.

Discussion

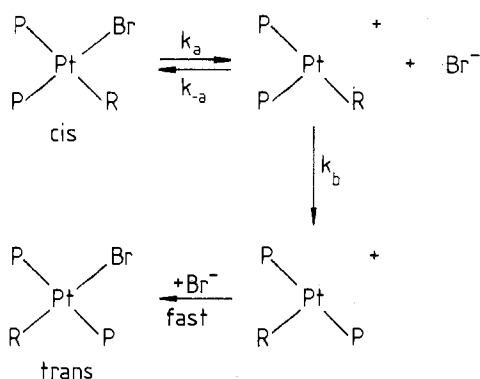
The rate and activation parameters for the spontaneous isomerization of *cis*-[Pt(PEt₃)₂(2,4,6-Me₃C₆H₂)Br] are in agreement with those reported elsewhere²⁵ (Table VI). Due to the observed mass law retardation of the isomerization by bromide, it was suggested²⁵ that the rate-determining step could involve the reversible dissociative release of bromide to

Table IV. Temperature and Pressure Dependence of k_{obsd} for the Reaction $\text{cis-}[\text{Pt}(\text{PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}] + \text{SC}(\text{NH}_2)_2$ in Methanol^a

temp, °C	pressure, bar	$k_{\text{obsd}} \times 10^4, \text{s}^{-1}$					$k_1 \times 10^4, \text{s}^{-1}$	$k_2 \times 10^3, \text{M}^{-1} \text{s}^{-1}$
		[SC(NH ₂) ₂], M						
		0.01	0.025	0.05	0.075	0.10		
22.9	1	1.12	1.46	2.10	2.51	3.06	1.11	2.01
		1.28	1.65	2.08	2.68	3.09		
34.0	1	3.93	4.29 ^b	5.48	6.75	7.72	3.45	4.28
38.85	1	6.07	7.01	8.39	10.2	11.7	5.40	6.29
45.4	1	11.2		14.9	17.5	20.0	10.1	9.81
30.0	1	2.52	3.01	3.95	4.88	5.50	2.25	3.25
		2.62	3.04	3.96	4.54	5.45		
	250	3.04	3.86	4.24	6.02	6.47	2.53	4.27
		2.86	3.44	4.93	5.57	7.11		
	500	3.56	4.35	5.49	6.85	7.84	3.08	4.82
		3.64	4.21	5.46	6.40	8.09		
	750	4.49	4.95	6.23	7.92	8.90	3.72	5.54
		4.45	5.08	6.19	8.08	9.72		
	1000	4.81	6.48	7.17	8.69	10.1	4.36	5.56
		4.70	5.60	6.90	8.26	9.86		
		for k_1					for k_2	
		$\Delta H^\ddagger, \text{kJ mol}^{-1}$					74.4 ± 0.7	
		$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$					-68.7 ± 2.2	
		$\Delta V_{\text{exp}}^\ddagger, \text{cm}^3 \text{mol}^{-1}$					-17.0 ± 0.7	
							52.9 ± 1.4	
							-117.4 ± 4.5	
							-13.3 ± 2.6	

^a [Pt(II)] = 1×10^{-4} M. ^b [SC(NH₂)₂] = 0.02 M.

Scheme I



yield a three-coordinate "cis-like" intermediate, which is then converted to a "trans-like" structure, followed by the uptake of bromide to give the trans product (see Scheme I in which P = PEt₃ and R = 2,4,6-Me₃C₆H₂). The rate law for this suggested mechanism is obtained from a steady-state treatment of the "cis-like" intermediate.²³

$$k_{\text{obsd}} = k_a k_b / \{k_{-a}[\text{Br}^-] + k_b\} \quad (1)$$

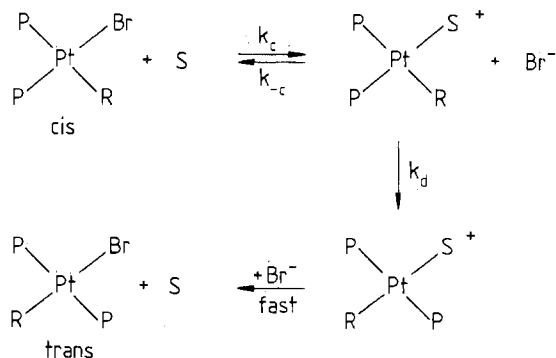
An alternative mechanism involves the reversible release of bromide during an associative attack by a solvent molecule, as outlined in Scheme II where P = PEt₃, R = 2,4,6-Me₃C₆H₂, and S = MeOH. The rate law for such a mechanism can be deduced in a similar way as for (1):

$$k_{\text{obsd}} = k_c k_d / \{k_{-c}[\text{Br}^-] + k_d\} \quad (2)$$

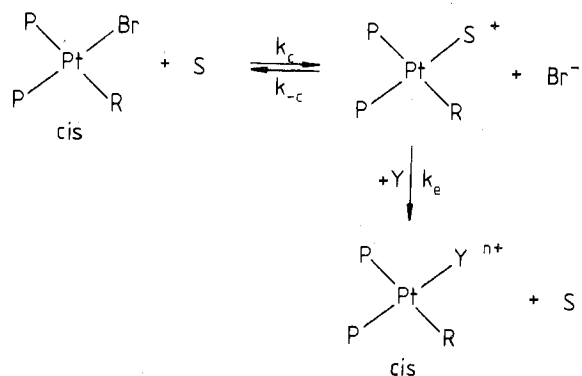
Both eq 1 and 2 are in agreement with the experimental data²⁵ since they demand that plots of k_{obsd}^{-1} vs. [Br⁻] be linear. Under our experimental conditions no bromide was added, so that eq 1 and 2 reduce to $k_{\text{obsd}} = k_b$ and $k_{\text{obsd}} = k_c$, respectively, such that the reported rate and activation parameters (Tables I and VI) are those for either k_a (dissociative process—Scheme I) or k_c (associative process—Scheme II). Before assignment of a definite mechanism to the spontaneous isomerization process, the data for the k_1 path of the substitution of the cis complex should be considered.

The values of k_1 for the reaction of $\text{cis-}[\text{Pt}(\text{PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}]$ with iodide and thiourea (Table VI) are very similar and close to that found here and in the literature²⁵ for

Scheme II



Scheme III



the isomerization reaction. The values of ΔH^\ddagger and ΔS^\ddagger for k_1 are in similar agreement with those for the isomerization reaction. A close correlation is also observed in the values of $\Delta V_{\text{exp}}^\ddagger$ for the k_1 path, and this will be discussed in detail later in the text. The k_1 path of the cis isomer may proceed via an associative type of mechanism, as outlined in Scheme III where P = PEt₃, R = 2,4,6-Me₃C₆H₂, S = MeOH, and Y = I⁻ ($n = 0$) or SC(NH₂)₂ ($n = 1$), so that the following rate law can be derived by applying the steady-state treatment to the solvated intermediate species.

$$k_{\text{obsd}} = k_c k_e [\text{Y}] / \{k_{-c}[\text{Br}^-] + k_e[\text{Y}]\} \quad (3)$$

Equation 3 reduces to $k_{\text{obsd}} = k_c$ in the absence of bromide,

Table V. Temperature and Pressure Dependence of k_{obsd} for the Reaction $\text{trans-[Pt(PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}] + \text{SC(NH}_2)_2$ in Methanol^a

temp, °C	pressure, bar	$k_{\text{obsd}} \times 10^4, \text{s}^{-1}$									$k_1 \times 10^4, \text{s}^{-1}$	$k_2 \times 10^2, \text{M}^{-1} \text{s}^{-1}$	
		[SC(NH ₂) ₂], M											
		0.002	0.005	0.010	0.015	0.020	0.025	0.050	0.075	0.10			
7.6	1			1.09			2.46	4.98	7.53	9.82	0.19 ± 0.17	1.00 ± 0.03	
				1.62			2.58	5.25	8.00	10.6			
12.0	1			1.71			3.54	6.65	10.1	12.9	0.50 ± 0.23	1.26 ± 0.04	
				1.44			3.87	7.63	9.42	13.2			
17.3	1			2.58			5.07	9.64	14.9	18.2	0.79 ± 0.42	1.79 ± 0.07	
22.9	1			3.48			7.84	14.2	20.9	27.7	1.13 ± 0.27	2.59 ± 0.05	
				3.56			7.71	14.3	19.9	26.3			
30.0	1			6.14			12.3	23.8	32.3		2.25 ± 0.42	4.14 ± 0.09	
				6.45			12.4	23.6	33.5				
15.0	1	0.651		2.00			4.51	8.72	12.7	16.3	0.39 ± 0.06	1.61 ± 0.01	
		0.587		1.95			4.38	8.45	12.5	16.4			
	250	0.650	1.32	2.24	3.31	4.33	4.84	8.30			0.59 ± 0.11	1.64 ± 0.05	
		0.628	1.38	2.33	3.33	3.73	4.63	9.03					
	500	0.817	1.56	2.68	3.39	4.93	5.49	9.43			0.72 ± 0.12	1.86 ± 0.05	
		0.834	1.58	2.69	3.49	4.53	5.73	10.2					
	750	0.952	1.76	2.97	3.66	5.49	6.08				0.57 ± 0.19	2.38 ± 0.13	
		0.963	1.68	3.04	5.00	5.37	6.62						
	1000	1.04	2.14	3.34	4.61	6.13	6.75				0.71 ± 0.12	2.59 ± 0.08	
		1.02	2.11	3.49	4.61	5.73	7.42						
						for k_1			for k_2				
						$\Delta H^\ddagger, \text{kJ mol}^{-1}$			71.1 ± 9.6			42.6 ± 1.7	
						$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$			-80 ± 33			-130.4 ± 5.8	
						$\Delta V^\ddagger_{\text{exp}}, \text{cm}^3 \text{mol}^{-1}$			-11.0 ± 5.7			-12.5 ± 2.0	

^a [Pt(II)] = 1 × 10⁻⁴ M.Table VI. Rate and Activation Parameters for Various Reactions of $\text{cis- and trans-[Pt(PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}]^a$ in Methanol

reaction	$k_1 \times 10^4, \text{s}^{-1} (30^\circ\text{C})$	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$	$\Delta V^\ddagger_{\text{exp}}, \text{cm}^3 \text{mol}^{-1} (30^\circ\text{C})$	$k_2 \times 10^4, \text{M}^{-1} \text{s}^{-1} (30^\circ\text{C})$	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$	$\Delta V^\ddagger_{\text{exp}}, \text{cm}^3 \text{mol}^{-1} (30^\circ\text{C})$	ref ^b
cis → trans-isomerization	1.90 ± 0.16	81.9 ± 1.6	-45.2 ± 5.5						
	1.9	67.3	-94.5						25
cis-[PtP ₂ RBr] + I ⁻	1.86 ± 0.05	75.9 ± 0.6	-64.0 ± 1.9	-14.1 ± 0.5					
	2.29 ± 0.04 ^c								
	1.9	66.9	-94.5						25
trans-[PtP ₂ RBr] + I ⁻	2.14 ± 0.03 ^c	79.6 ± 1.1	-52.3 ± 3.5	-15.8 ± 0.4	4.59 ± 0.50 ^c	59 ± 10	-115 ± 33	-16.4 ± 5.4	
	4.34 ± 0.61	70.6 ± 4.2	-76.9 ± 8.3						20 ^d
cis-[PtP ₂ RBr] + SC(NH ₂) ₂	2.25 ± 0.06	74.4 ± 0.7	-68.7 ± 2.2	-17.0 ± 0.7	32.5 ± 1.0	52.9 ± 1.4	-117.4 ± 4.5	-13.3 ± 2.6	
trans-[PtP ₂ RBr] + SC(NH ₂) ₂	2.25 ± 0.42	71.1 ± 9.6	-80 ± 33	-11.0 ± 5.7 ^e	414 ± 9	42.6 ± 1.7	-130.4 ± 5.8	-12.5 ± 2.0 ^e	
				-17.2 ± 0.0 ^f				-11.4 ± 0.1 ^f	
	3.99	70.6 ± 4.2	-76.9 ± 8.3		494	34.3	-157.2		20 ^d

^a Abbreviated as PtP₂RBr in the table. ^b Data reported in this work unless otherwise indicated. ^c Determined at 10 bar. ^d Data reported for the corresponding chloro complex. ^e temp = 15 °C. ^f Estimated according to the procedure outlined in the Results section, temp = 15 °C.

Table VII. Rate and Activation Parameters for the Isomerization and Solvolysis of $\text{cis-[Pt(PEt}_3)_2\text{RBr}]$ in Methanol, Taken from the Data of Romeo et al.²²

R	$k_{\text{iso}} \times 10^3, \text{s}^{-1} (30^\circ\text{C})$	$\Delta H^\ddagger_{\text{iso}}, \text{kJ mol}^{-1}$	$\Delta S^\ddagger_{\text{iso}}, \text{J K}^{-1} \text{mol}^{-1}$	$k_1 \times 10^3, \text{s}^{-1} (30^\circ\text{C})$	$\Delta H_1^\ddagger, \text{kJ mol}^{-1}$	$\Delta S_1^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$	$k_d \times 10^3, \text{s}^{-1} (30^\circ\text{C})$	$K_c \times 10^4, \text{M} (30^\circ\text{C})$	$k_{-c} (=k_c/K_c), \text{M}^{-1} \text{s}^{-1}$
C ₆ H ₅	1.07	87.8	-12.5	6000	51.4	-59.3	1.43	0.69	8.60 × 10 ⁴
<i>p</i> -MeC ₆ H ₄	2.34	81.5	-25.9	4280	47.6	-75.2	2.27	0.75	5.86 × 10 ⁴
<i>o</i> -MeC ₆ H ₄	0.72	98.6	+20.9	54.4	51.8	-97.8	0.66	0.73	7.42 × 10 ²
<i>o</i> -EtC ₆ H ₄	0.55	100.3	+23.8	16.2	54.3	-98.6	0.99	0.49	3.24 × 10 ²
2,4,6-Me ₃ C ₆ H ₂	0.19	67.3	-94.5	0.19	66.9	-94.5	0.20	2.1	9.04 × 10 ⁻¹

^a Data reported in Table V of ref 25. ^b Calculated from the data in Table II of ref 25; see Discussion.

such that the reported values and activation parameters for k_1 (Table VI) are those for k_c in Scheme III. Assuming that the rate-determining step for isomerization and substitution (k_1 path) is the solvolysis reaction, then $k_c[Y] \gg k_d$, since the substitution process proceeds with complete retention of configuration.²⁵

The strongly negative ΔS^\ddagger values (Table VI) for the above-mentioned reactions certainly tend to favor a basically associative mechanism. This interpretation is in disagreement with that of Romeo and co-workers,^{24,25} who interpreted their

data according to a dissociative mechanism for the solvolysis and isomerization of $\text{cis-[Pt(PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}]$. A comparison of their rate and activation parameters for the isomerization of a series of $\text{cis-[Pt(PEt}_3)_2\text{RBr}]$ complexes with that found for the solvolysis (k_1 path) reaction (see data reproduced in Table VII) demonstrates that substantial differences exist, with the exemption of R = mesityl. Since it is generally accepted^{4,5,6,25} that solvolysis of the less sterically hindered complexes (i.e., R = C₆H₅, *p*-MeC₆H₄, *o*-MeC₆H₄, and *o*-EtC₆H₄) proceeds via an associative mechanism, the

above-outlined deviations were interpreted as evidence for a dissociative isomerization process.²³ However, it is more logical that increasing steric crowding will *enhance* dissociative reactions^{34,35} or inhibit associative ones. Nevertheless, due to the good agreement between the rate and activation parameters for the isomerization and k_1 path of the mesityl complex (see data in Table VII), it is understandable that Romeo et al.²⁵ concluded that substitution of the cis mesityl complex must also be dissociative in character. We, however, prefer the following alternative way of interpreting their data (Table VII), in line with our arguments for an associative mechanism.

The solvolysis reaction for the less sterically hindered complexes is sufficiently fast that this step can be considered as a preequilibrium in the isomerization process similar to that outlined in Scheme II. The rate expression now becomes

$$k_{\text{obsd}} = k_d K_c / \{[\text{Br}^-] + K_c\} \quad (4)$$

where $K_c = k_c/k_{-c}$. In the absence of added bromide eq 4 simplifies to $k_{\text{obsd}} = k_d$, which means that under such circumstances the measured rate constant refers to the isomerization process of the solvated intermediate (k_d), not to solvolysis (k_c). We repeat that this treatment will only be valid under circumstances where k_c and $k_{-c} \gg k_d$. By use of the data of Romeo et al.²⁵ for the isomerization as a function of $[\text{Br}^-]$ (taken from Table II in ref 25), it is possible to estimate the values of K_c and k_d from plots of k_{obsd}^{-1} vs. $[\text{Br}^-]$ (see Table VII). Combining the values for k_c (equal to k_1 in Table VII) with K_c , it is possible to calculate k_{-c} ($= k_c/K_c$). From a comparison of the values of k_c , k_{-c} , and k_d in Table VII, it follows that the above treatment is valid for all complexes (i.e., $k_c, k_{-c} \gg k_d$) except for the case where R = mesityl. In the latter, k_c and k_d are of similar magnitude such that an equilibrium treatment of the solvolysis reaction is not valid, and the steady-state treatment, as outlined with eq 2, must be adopted, leading to $k_{\text{obsd}} = k_c$. We must therefore conclude that the rate and activation parameters for the isomerization of the less sterically hindered complexes (all entries in Table VII, excluding R = mesityl) are those for k_d as the rate-determining step and, being composites of K_c and k_d , differ considerably from those for k_c . This explains the insensitivity of k_{iso} to variations in R and the completely different activation parameters found for these reactions. The slight differences between k_{iso} and k_d in Table VII are due to the fact that they have been taken from two different sets of data. With the natural exception of R = mesityl, the values of K_c seem to be fairly constant for various R substituents indicating that k_c and k_{-c} are equally influenced by steric factors. The k_{-c} reaction is extremely fast (even at very low $[\text{Br}^-]$) for less sterically hindered systems, with the result that K_c is very small.

We now turn to a discussion of the other reactions studied in this investigation. The rate and activation parameters for the solvolysis (k_1 path) of the trans isomer are in good agreement with earlier findings for the corresponding chloro system²⁰ and compare remarkably well with those reported for the solvolysis and isomerization of the cis isomer (Table VI). This insensitivity to the nature of the leaving group once again points to an associative mechanism for k_1 . The similarity in the rate and activation parameters for the two isomers is not reconcilable with the concept of a dissociative mechanism caused by increased crowding of the leaving group cis to the bulky mesityl group. Whereas within the framework of a basically associative mechanism, analogous to that outlined in Scheme III, the transition states originating from either cis or trans species would be subjected to similar steric crowding, leading in turn to comparable reaction rates and activation parameters.

On the other hand, the direct (bimolecular) attack (i.e., the k_2 path) is extremely sensitive to the position of the mesityl

group. For instance, despite the relative strength of the large iodide ligand ($n_{\text{Pt}} = 5.46^{36}$), no direct attack on the cis isomer was found.²⁵ For a stronger nucleophile, such as thiourea ($n_{\text{Pt}} = 7.1^{36}$), the k_2 path represents a substantial contribution to k_{obsd} for the cis form. Thus, as shown for the analogous reactions of the sterically crowded $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]^+$ complexes,⁹ the primary rate-determining factors for an associative attack appear to be the size and the nucleophilicity of the potential ligands. The extremely weak ($n_{\text{Pt}} = 0^{36}$), but comparatively small, methanol molecule can therefore overcome the steric hindrance with greater ease. If a dissociative mechanism were to operate, the far less sterically restricted three-coordinate intermediate would not be expected to show such selectivity to the size of the incoming ligand, with the result that k_2 should dominate over k_1 .

A small, but significant, k_2 path is found for the reaction of *trans*- $[\text{Pt}(\text{PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}]$ with iodide, while the reaction with thiourea proceeds practically through the k_2 path. The decrease in ΔH^\ddagger for k_2 down the reaction series in Table VI is attributable to the nucleophilicity of the entering nucleophile and the steric crowding at the Pt(II) reaction center.

Generally $\Delta V_{\text{exp}}^\ddagger$ can be considered as consisting of two components:^{26,27,37} an intrinsic part, $\Delta V_{\text{intr}}^\ddagger$, and a solvation part, $\Delta V_{\text{solv}}^\ddagger$. $\Delta V_{\text{intr}}^\ddagger$ reflects the volume changes due to the variations in bond lengths and angles during the formation of the transition state, while $\Delta V_{\text{solv}}^\ddagger$ arises from changes in solvation during this process. In the case of a dissociative mechanism, $\Delta V_{\text{intr}}^\ddagger$ will be positive due to bond cleavage, while $\Delta V_{\text{solv}}^\ddagger$, stemming from an increase in electrostriction associated with the development of two ions in the transition state, will be negative. Calculations based on the creation of point charges within a cavity in methanol predict³⁸ a $\Delta V_{\text{solv}}^\ddagger$ value of $-8 \text{ cm}^3 \text{ mol}^{-1}$. This has been substantiated by high-pressure measurements³⁹ on the Menshutkin reaction in which partial charge separation is observed. It follows that the overall $\Delta V_{\text{exp}}^\ddagger$ for a purely dissociative mechanism should be approximately zero, which is certainly not in accord with the observed $\Delta V_{\text{exp}}^\ddagger$ values for the k_1 path shown in Table VI. On the other hand, an associative mechanism will mainly involve a negative contribution from $\Delta V_{\text{intr}}^\ddagger$ due to bond formation and only a minor contribution from $\Delta V_{\text{solv}}^\ddagger$ since uncharged species are involved. Thus the overall $\Delta V_{\text{exp}}^\ddagger$ will be negative with a maximum conceivable value of $-40.7 \text{ cm}^3 \text{ mol}^{-1}$, i.e., the partial molar volume of methanol. Obviously contributions from bond stretching and incomplete bond formation will lead to smaller $\Delta V_{\text{exp}}^\ddagger$ values. It is interesting to note that the $\Delta V_{\text{exp}}^\ddagger$ value for the solvolysis of $[\text{Pd}(\text{Et}_4\text{dien})\text{I}]^+$ in methanol,⁴⁰ which is thought to proceed via an I_a mechanism, is $-11.7 \text{ cm}^3 \text{ mol}^{-1}$ and is close to the values for the k_1 path in Table VI. Thus, we prefer to interpret our results as mainly reflecting the values of $\Delta V_{\text{intr}}^\ddagger$, thereby strongly supporting our other arguments for an associative type of mechanism as outlined in Scheme III. The absence of a detectable pressure dependence of $\Delta V_{\text{exp}}^\ddagger$ emphasizes the importance⁴¹ of $\Delta V_{\text{intr}}^\ddagger$ and may be interpreted⁹ as a further indication that the associative mechanism is of the I_a type, rather than A. However, this evidence is by no means conclusive.

The values of ΔS^\ddagger and $\Delta V_{\text{exp}}^\ddagger$ for k_2 (Table VI) are, within experimental error limits, fairly constant for the three reactions reported. This insensitivity to the charge on the entering nucleophile is not surprising as the *overall* charge remains constant throughout the activation process. We conclude that $\Delta V_{\text{exp}}^\ddagger$ also largely represents the value of the pressure-independent $\Delta V_{\text{intr}}^\ddagger$ and is therefore considered as evidence for an associative mechanism, in line with the values of ΔS^\ddagger . The latter are more negative than those reported for the k_1 path, probably due to the larger steric hindrance encountered by iodide and thiourea as compared to methanol. The possibility

is not ruled out that the entering nucleophile is already weakly coordinated to the complex ion in the ground state and that the substitution process follows an interchange path as described by an I_a mechanism. Similar data⁹ have previously been considered as evidence for an I_a mechanism in the substitution reactions of $[Pt(\text{dien})X]^+$ complexes, where dien = diethylenetriamine and $X^- = Br^-, Cl^-, I^-, \text{ and } N_3^-$.

To sum up, we conclude that the isomerization reaction of *cis*- $[Pt(\text{PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}]$ and the substitution reactions (k_1 and k_2 paths) of *cis*- and *trans*- $[Pt(\text{PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}]$ all proceed via an associative type of mechanism. A definite conclusion as to whether the mechanisms are of the A or I_a type cannot be made, although it is hoped that the results of the solvent dependence study presently in progress will provide more detail on the intimate mechanism involved.

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Registry No. *cis*- $[Pt(\text{PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}]$, 22289-37-8; *trans*- $[Pt(\text{PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}]$, 68681-91-4; I^- , 20461-54-5; thiourea, 62-56-6.

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Contribution from the Chemistry Department,
Monash University, Clayton, Victoria, Australia 3168

Rates of Electron-Transfer Reactions of Some Copper(II)-Phenanthroline Complexes with Cytochrome c(II) and Tris(phenanthroline)cobalt(II) Ion

MARY ANN AUGUSTIN and JOHN K. YANDELL*

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Rate constants for the one-electron oxidation of horse heart cytochrome *c*(II) (ferrocytochrome *c*) by aquated bis(1,10-phenanthroline)copper(II) ion, bis(2,9-dimethyl-1,10-phenanthroline)copper(II) ion, and bis(5-nitro-1,10-phenanthroline)copper(II) ion were found to be $(2.72 \pm 0.26) \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$, $(1.00 \pm 0.04) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, and $(1.57 \pm 0.06) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, respectively, in aqueous solution at pH 6.1, at 25 °C, and at an ionic strength of 0.1 M. Activation enthalpies, $\Delta H^\ddagger = 55, 16, \text{ and } 46 \text{ kJ mol}^{-1}$, and activation entropies, $\Delta S^\ddagger = -33, -77, \text{ and } -50 \text{ J mol}^{-1} \text{ K}^{-1}$, were also measured for the same reactions. The rate constant and activation parameters for the one-electron oxidation of tris(1,10-phenanthroline)cobalt(II) ion by bis(2,9-dimethyl-1,10-phenanthroline)copper(II) ion were found to be $(8.8 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 43 \text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = -6 \text{ J mol}^{-1} \text{ K}^{-1}$ under the same conditions. These results are discussed in terms of a "structural barrier" to electron transfer, which is a consequence of the difference in coordination number and stereochemistry between the copper(II) reactants and the copper(I) products.

Introduction

Copper(II)-copper(I) redox reactions are unusual in that, at least for "simple" copper complexes, the coordination number and stereochemistry of the two oxidation states differ. Copper(II) complexes in aqueous solution are usually thought to be six-coordinate and tetragonal, whereas copper(I) complexes prefer four-coordinate, tetrahedral coordination. This may be an oversimplification since in the solid state

Cu(II) is frequently found to be five-coordinate¹ and Cu(I) exhibits some tendency toward linear two-coordinate. In any event, in water, Cu(II) complexes are likely to have a higher coordination number (including solvent ligands). A classic manifestation of this difference was reported by James and Williams² in 1961. They found that the methyl substituents in 2,9-dimethyl-1,10-phenanthroline (dmphen) greatly decreased the stability of the $\text{Cu}(\text{dmphen})_2^{2+}$ but increased