

tion of these values is scarcely possible. However, the values are consistent with the suggestions that  $\Delta H^\ddagger$  for the rhodium system may include a significant contribution from energy terms of a type common to substitution at the metal center, such as rhodium-oxygen bond stretching, and that the difference in the  $\Delta S^\ddagger$  values for the two reactions could in part be a reflection of a lower charged transition state for rhodium, with consequent greater freedom for solvent, and in part an indication for chromium of rather specific geometric requirements for the transition state. If it were not for the relatively large positive value of  $\Delta S^\ddagger$  for the  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$ -Ce(IV) system, this reaction would proceed many orders of magnitude more slowly than the corresponding  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$  reaction.

It is relevant to inquire if the components  $\text{M}(\text{C}_2\text{O}_4)_3^{2-}$ , produced on electron transfer to the Ce(IV), are most appropriately described as complexes in which M remains in oxidation state +3 (*i.e.*,  $d^3$  or  $d^6$  complexes, each containing a coordinated oxalate radical ion) or complexes where M is in the oxidation state +4 (*i.e.*,  $d^2$  or  $d^5$  complexes). These distinctions are chemically meaningful, although, for the transient species under consideration, not easily made.<sup>36</sup> De-

(36) It is recognized that in some cases the oxidation state of a central atom in a complex may be difficult to specify in other than an arbitrary way. This situation arises especially where electrons may be considered to be delocalized over a large part of the complex. For most isolable complexes of chromium and rhodium there is little ambiguity in the oxidation state of the metal, but the situation is less clear for highly reactive intermediates, such as  $\text{Cr}(\text{C}_2\text{O}_4)_3^{2-}$ , etc. In certain cases direct distinctions between extreme possibilities are, at least in principle, feasible. Thus the number of unpaired electron spins for  $\text{Cr}(\text{C}_2\text{O}_4)_3^{2-}$  would depend on whether it is a complex of Cr(IV) or of Cr(III) associated with an oxalate radical ion.

tailed consideration of electrode potentials for Cr(IV)-Cr(III) and Rh(IV)-Rh(III) couples,<sup>37-41</sup> while not leading to unambiguous conclusions, suggests that the one-electron oxidations of the  $\text{Cr}^{3+}$  and  $\text{Rh}^{3+}$  metal centers are unlikely to be particularly favorable from a thermodynamic standpoint. Free oxalate is efficiently oxidized in sulfuric acid by both Ce(IV) and Mn(III), however, and it seems to us more likely that the initial one-electron oxidations of  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$  and  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$  will involve oxidation of a coordinated oxalate to a radical ion. Undoubtedly coordination to the chromium and rhodium centers would polarize the oxalate electrons and make it more difficult, in both a thermodynamic and a kinetic sense, for an external oxidant to be effective. For identical coordination such polarization should be greater in the case of rhodium where metal-ligand bonds are likely to have more covalent character. The difference in polarization would certainly be greater still if bridging oxalate is chelated to the rhodium and coordinated to the chromium by only a single oxygen. Also, for an electron transfer from an oxalate, as for transfer from an inert metal center, some prior metal-oxygen bond adjustment may be required which would involve larger energy requirements in the case of the rhodium. In view of these likely contributions the observed order of reactivity  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-} > \text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$  is not surprising.

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CONTRIBUTION FROM ISTITUTO DI CHIMICA FISICA,  
UNIVERSITÀ DI MESSINA, MESSINA 98100, ITALY

## Substitution Reactions of the Sterically Hindered *trans*-Bis(triethylphosphine)chloro(mesityl)platinum(II)

By G. FARAONE, V. RICEVUTO, R. ROMEO, AND M. TROZZI

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Kinetic data for substitution reactions of *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(ms)Cl (ms = mesityl) with various nucleophiles in methanol and dimethyl sulfoxide are reported. The results are discussed in terms of a balance between steric factors and electronic structure in determining the reaction mechanism. Depending on the solvent and nucleophile, the kinetic behavior is similar either to that found for "pseudooctahedral" complexes or to the associative mechanism typical of square-planar substitution reactions.

### Introduction

In substitution reactions of low-spin  $d^8$  systems, both steric factors and electronic structure favor an associative mechanism. Thus, the central metal atom is exposed for attack above and below the (square) plane and has a vacant  $p_z$  orbital, of relatively low

energy, available for a  $\sigma$  bond in forming the transition state.<sup>1,2</sup>

It has recently been pointed out that in sterically

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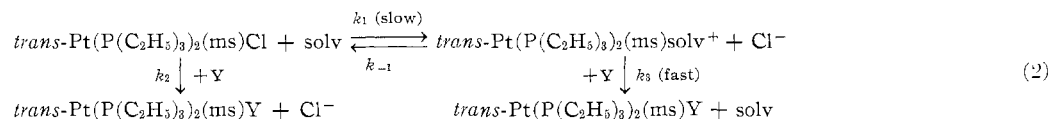
hindered complexes of type Pd(amine) $X^+$  (amine = Et<sub>4</sub>dien, MeEt<sub>4</sub>dien, or Me<sub>5</sub>dien), the direct bimolecular displacement seems unlikely and it would appear that the reaction proceeds by a dissociative process, similar to that found for octahedral complexes.<sup>3-5</sup> Therefore it is reasonable to assume that the steric factors are going to dominate the electronic structure in determining the mechanism.

We have studied the substitution reactions of *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(ms)Cl with various entering groups in methanol and dimethyl sulfoxide. In these compounds the aromatic ring is forced to maintain its plane perpendicular to that of the complex and the two methyl groups, above and below the plane, will hinder the reaction center less effectively than the substituted amines.<sup>6</sup>

### Experimental Section

**Materials.**—The complex *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(ms)Cl was prepared by following the method reported in the literature<sup>7,8</sup> and was characterized by analysis; mp 196–197°. *Anal.* Calcd for C<sub>21</sub>H<sub>41</sub>ClP<sub>2</sub>Pt: C, 43.05; H, 7.05; MW, 58 6.09. Found: C, 43.0; H, 7.25; MW (osmometrically in benzene solution), 582.

All other materials used were of reagent grade. Li<sup>36</sup>Cl was



obtained by isotopic exchange with H<sup>36</sup>Cl (Sorin, 50  $\mu$ Cl/ml) in methanol solution and recrystallized from acetone. Absolute methanol was dried and purified by distillation after refluxing over Mg(OCH<sub>3</sub>)<sub>2</sub>.<sup>9</sup> Dimethyl sulfoxide was fractionated under reduced nitrogen pressure.<sup>10</sup>

**Kinetics.**—The reaction rates (except those with <sup>36</sup>Cl<sup>-</sup>) were followed spectrophotometrically in the ultraviolet region (240–310  $m\mu$ ) by using an Optica CF-4 recording apparatus or a Beckman DU. The details of experimental procedure have been given in a previous paper.<sup>11</sup>

The concentrations of the reagent Y<sup>-</sup> exceeded the complex concentration (at least 10:1), in order to provide pseudo-first-order conditions. The ionic strength was kept constant by adding LiClO<sub>4</sub>, even though, for this uncharged complex, a primary salt effect can be excluded.

In many cases the reaction spectra showed well-defined isosbestic points, indicating that only the substrate and the product are the absorbing species. The completeness of the reaction was checked by comparing the final spectra obtained at various reagent concentrations.

The rate data are listed in Tables I and II.

**Isotopic Exchange Method.**—Solutions of *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(ms)<sup>36</sup>Cl and LiCl were mixed in the required volumes and thermostated at 30 or 45  $\pm$  0.1°. At intervals aliquots were taken from the reaction mixture, and the complex was separated from uncomplexed chloride by making use of an anion-exchange resin, Dowex 1X4 (50–100 mesh), nitrate form.<sup>12</sup> The solution activity

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of the liquid samples was determined by means of a liquid-type Geiger-Müller counter.

The least-squares method was applied to experimental data. The exchange rates obtained were analyzed by means of the well-known McKay law for simple exchange reactions.<sup>13</sup> The results are listed in Table III.

### Discussion

The variation of the pseudo-first-order rate constants,  $k_{\text{obsd}}$ , with the reagent concentration (Figure 1) was consistent with the two-term rate law which is usual for square-planar substitutions,<sup>14</sup> *i.e.*

$$k_{\text{obsd}} = k_1 + k_2[Y] \quad (1)$$

It is noteworthy that for all entering groups examined, only CN<sup>-</sup>, SeCN<sup>-</sup>, and SC(NH<sub>2</sub>)<sub>2</sub> exhibit a significant  $k_2$  value. N<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, and even good nucleophiles such as I<sup>-</sup>, SCN<sup>-</sup>, and C<sub>6</sub>H<sub>5</sub>S<sup>-</sup> show a rate independent (in the range 10<sup>-3</sup> to 10<sup>-1</sup> M) of the nature and concentration of the reagent. The behavior of these last nucleophiles strongly suggests that a dissociative mechanism is operative in the rate-determining step of the reaction. The experimental evidence supports mechanism 2.

According to the two-term rate law (eq 1) the reaction proceeds by means of two competing paths. The  $k_2$  term refers, as usual, to a direct bimolecular displacement of Cl<sup>-</sup> by Y<sup>-</sup>. The  $k_1$  term is in agreement with a solvent-assisted dissociative process, as suggested for pseudooctahedral complexes.<sup>4</sup> The steric configuration of *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(ms)Cl accounts for the kinetic behavior. The two methyl groups above and below the plane of the complex, shielding the reaction center, reduce the possibility of direct attack on the complex by poor nucleophiles. Therefore the reaction proceeds essentially *via*  $k_1$  and the Pt-Cl bond breaking is the rate-determining step, followed by the fast entry of Y<sup>-</sup>. On the other hand, the steric configuration of the complex and the fact that good nucleophiles failed to react directly make an associative mechanism *via*  $k_2$ , involving specifically one molecule of solvent as reactant, unlikely.

It is well known that for unhindered complexes of platinum(II), the solvolytic rate constant  $k_1$  is consistently larger in dimethyl sulfoxide than in methanol, owing to the different solvent nucleophilicity.<sup>2,12,15,16</sup>

In our system the  $k_1$  value (Table IV) is greatly reduced in going from the protic to the dipolar aprotic solvent. This is consistent with the hypothesis of a mechanism in which bond breaking of the leaving

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TABLE I<sup>a</sup>  
PSEUDO-FIRST-ORDER RATE CONSTANTS  $k_{\text{obsd}}$  (SEC<sup>-1</sup>) FOR THE REACTION  
 $\text{trans-Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2(\text{ms})\text{Cl} + \text{Y}^- \longrightarrow \text{trans-Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2(\text{ms})\text{Y} + \text{Cl}^-$   
IN METHANOL AT 30 AND 45°

Entering group Y <sup>-</sup>	Temp, °C	Concn × 10 <sup>3</sup> , M	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	Entering group Y <sup>-</sup>	Temp, °C	Concn × 10 <sup>3</sup> , M	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	Entering group Y <sup>-</sup>	Temp, °C	Concn × 10 <sup>3</sup> , M	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup>
N <sub>3</sub> <sup>-</sup>	30	0.63	4.81	SCN <sup>-</sup>	30	0.63	4.24	SeCN <sup>-</sup>	30	0.50	4.32
		1.00	4.82			1.00	3.81			0.75	5.05
		1.25	4.74			1.25	3.55			1.25	5.63
		2.50	5.15			2.50	3.88			2.50	7.52
		5.00	4.69			5.00	4.00			5.00	11.40
Br <sup>-</sup>	30	1.00	3.40	C <sub>6</sub> H <sub>5</sub> S <sup>-</sup>	30	0.63	3.92		45	0.50	18.00
		1.25	3.45			1.00	3.88			0.75	18.80
		2.50	3.77			1.25	4.19			1.25	21.00
		5.00	3.66			2.50	4.08			2.50	25.00
		7.50	3.42			5.00	4.53			5.00	14.80
I <sup>-</sup>	30	10.00	3.48	CN <sup>-</sup>	30	10.00	4.87	SC(NH <sub>2</sub> ) <sub>2</sub>	30	10.00	17.80
		0.63	5.39			0.60	3.89			0.50	6.24
		1.00	4.60			1.00	4.71			0.75	8.04
		1.25	4.04			2.00	5.46			1.25	10.40
		2.50	4.79			4.00	6.93			2.50	16.00
NO <sub>2</sub> <sup>-</sup>	30	5.00	4.11		45	6.00	8.19		45	5.00	27.90
		7.50	3.62			8.00	10.40			7.50	42.40
		10.00	3.85			10.00	12.30			10.00	52.80
		0.63	4.00			0.60	16.80			0.50	19.4
		1.00	4.20			1.00	16.45			0.75	24.2
	45	2.50	4.23		45	2.00	18.53		45	0.50	19.4
		5.00	3.89			4.00	21.28			0.75	24.2
		7.50	3.61			6.00	24.08			1.25	28.6
		10.00	3.66			8.00	27.92			2.50	43.8
		0.50	14.96			10.00	30.41			5.00	63.2
		1.00	16.16			7.50	42.40			7.50	87.0
		2.50	14.87								
		5.00	15.38								

<sup>a</sup> Complex concentration was about  $2.5 \times 10^{-4} M$ ; ionic strength was kept constant at 0.1 M (LiClO<sub>4</sub>), except for Y<sup>-</sup> = <sup>36</sup>Cl<sup>-</sup>, CN<sup>-</sup>, and SeCN<sup>-</sup>. The experimental uncertainty in  $k_{\text{obsd}}$  values is about 15%.

TABLE II<sup>a</sup>  
PSEUDO-FIRST-ORDER RATE CONSTANTS  $k_{\text{obsd}}$  (SEC<sup>-1</sup>) FOR THE REACTION  
 $\text{trans-Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2(\text{ms})\text{Cl} + \text{Y}^- \longrightarrow \text{trans-Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2(\text{ms})\text{Y} + \text{Cl}^-$   
IN DIMETHYL SULFOXIDE AT 30 AND 45°

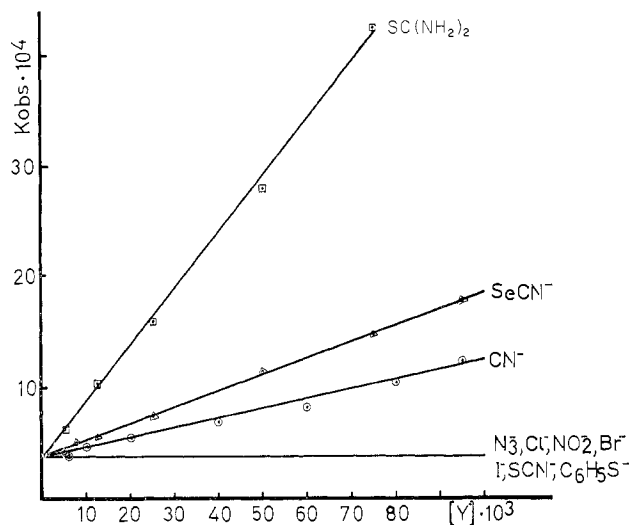
Entering group Y <sup>-</sup>	Temp, °C	Concn × 10 <sup>3</sup> , M	10 <sup>6</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	Entering group Y <sup>-</sup>	Temp, °C	Concn × 10 <sup>3</sup> , M	10 <sup>6</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	Entering group Y <sup>-</sup>	Temp, °C	Concn × 10 <sup>3</sup> , M	10 <sup>6</sup> k <sub>obsd</sub> , sec <sup>-1</sup>
N <sub>3</sub> <sup>-</sup>	30	0.50	5.49	SCN <sup>-</sup>	30	0.50	6.07	SeCN <sup>-</sup>	30	0.50	10.5
		1.00	5.39			1.00	6.52			1.00	14.9
		2.50	5.41			2.50	7.38			2.50	25.6
		5.00	5.75			5.00	10.02			5.00	47.3
I <sup>-</sup>	30	7.50	7.11		45	7.50	13.30		45	0.75	41.2
		10.00	7.75			10.00	15.50			1.50	53.4
		0.50	5.63			0.50	25.8			2.00	64.3
		1.00	5.73			1.00	25.1			4.00	100.0
		2.50	6.04			2.50	29.3				
	45	5.00	6.42		45	5.00	37.5	SC(NH <sub>2</sub> ) <sub>2</sub>	30	0.50	54.7
		7.50	7.11			7.50	40.3			1.00	113
		10.00	7.75			10.00	46.5			2.50	268
		0.50	22.9							5.00	489
		1.00	23.1								
	45	2.50	25.7						45	0.50	128
		5.00	26.8			1.00	264				
						2.50	568				
						5.00	1170				

<sup>a</sup> Complex concentration was about  $2.5 \times 10^{-4} M$ ; ionic strength was kept constant at 0.1 M (LiClO<sub>4</sub>) except for Y<sup>-</sup> = <sup>36</sup>Cl<sup>-</sup> and SeCN<sup>-</sup>. The experimental uncertainty in  $k_{\text{obsd}}$  values is about 15%.

TABLE III

ISOTOPIC EXCHANGE KINETICS OF *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(ms)Cl WITH LiCl (a) IN METHANOL AT 30° AND (b) IN DIMETHYL SULFOXIDE AT 30 AND 45°

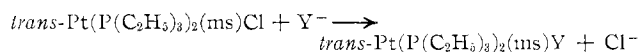
Part a			Part b		
Reagent concn × 10 <sup>2</sup> , M	Complex concn × 10 <sup>2</sup> , M	10 <sup>3</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	Reagent concn × 10 <sup>2</sup> , M	Complex concn × 10 <sup>2</sup> , M	10 <sup>3</sup> k <sub>obsd</sub> , sec <sup>-1</sup>
					30°
1.00	0.10	4.06	0.75	0.10	5.14
1.00	0.20	3.91	2.50	0.10	5.44
0.75	0.10	4.32	5.00	0.10	5.39
1.07	0.10	4.30	7.50	0.10	5.58
2.00	0.10	3.93			45°
4.00	0.10	4.15	0.75	0.13	20.20
6.00	0.10	3.60	1.00	0.13	21.50
			2.50	0.13	21.90
			5.00	0.13	23.70

Figure 1.—Plot of  $k_{\text{obsd}}$  vs. reagent concentration for reactions of *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(ms)Cl with various nucleophiles in methanol at 30°.

group is more important than bond making with a solvent molecule. The solvation of the leaving anion seems the major factor determining the rate of solvolysis. The methanol is more effective than dimethyl sulfoxide in helping to break the bond in the rate-determining step, because of the possibility of forming hydrogen bonds with a small and highly charged anion such as Cl<sup>-</sup>.<sup>17</sup> In methanol at 30° the substitution rate with SCN<sup>-</sup> undergoes a mass law retardation by chloride. The  $k_{\text{obsd}}$  value is reduced to  $1.26 \times 10^{-4}$  sec<sup>-1</sup> in a solution  $5 \times 10^{-3}$  M in NaSCN and 0.1 M in LiCl and further reduced to  $6.41 \times 10^{-5}$  sec<sup>-1</sup> where the LiCl concentration is raised to 0.25 M. It has already been pointed out<sup>18</sup> for the unhindered complex *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)Cl that the  $k_1$  term indicates which mechanism is operating—a dissociative one or an associative one with the solvent.

The dependence of the rate on the concentration

of CN<sup>-</sup>, SeCN<sup>-</sup>, or SC(NH<sub>2</sub>)<sub>2</sub> shows there is not such steric hindrance as to prevent a direct bimolecular displacement. In this case it is possible that the incoming group can use the vacant p<sub>z</sub> orbital on the central metal atom. It is known that these entering groups have large nucleophilic reactivity constants<sup>19</sup> and present a biphilic behavior toward platinum(II) complexes<sup>20</sup> for possible  $\pi$  interactions with the filled d orbitals of the metal. This results in a stabilization of the five-coordinate transition state and then makes an associative mechanism easier. The  $k_2$  value in the

TABLE IV<sup>a</sup>RATE CONSTANTS  $k_1$  (SEC<sup>-1</sup>) AT 30 AND 45° AND ACTIVATION PARAMETERS FOR THE REACTION

Temp, °C	10 <sup>3</sup> k <sub>1</sub> , sec <sup>-1</sup>	$\Delta H_1^\ddagger$ , kcal/mol	$\Delta S_1^\ddagger$ , eu
Methanol Solvent			
30	4.05		
45	15.25	16.9 ± 1	-18.4 ± 2
Dimethyl Sulfoxide Solvent			
30	0.055		
45	0.234	18.6 ± 1	-21.8 ± 2

<sup>a</sup> The rate constants  $k_1$  (sec<sup>-1</sup>) are the mean of the values reported above (Tables I-III) and of those obtained graphically by extrapolation, where a  $k_2$  value is evident. The mean error in  $k_1$  values is about ±4%.

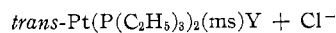
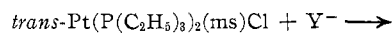
reaction with SC(NH<sub>2</sub>)<sub>2</sub> in methanol at 30° is about 100 times smaller for the hindered *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(ms)Cl than for the unhindered *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)Cl.<sup>18</sup>

As shown in Figure 2 a  $k_2$  term is evident even for I<sup>-</sup> and SCN<sup>-</sup> in dimethyl sulfoxide. Owing to the reduced effectiveness of the reaction to proceed *via* a  $k_1$  path in this dipolar aprotic solvent, a bimolecular contribution is then possible for these nucleophiles.

In Tables IV and V are reported the rate constant values  $k_1$  (sec<sup>-1</sup>) and  $k_2$  (M<sup>-1</sup> sec<sup>-1</sup>) for the reactions examined. (The  $k_1$  and  $k_2$  values have been obtained graphically as intercept and slope of the diagrams shown in Figures 1 and 2.)

The activation enthalpy is larger and the entropy less negative for the  $k_1$  path than for the reagent path ( $k_2$ ). The negative activation entropy for the dissociative path ( $k_1$ ) can be explained in terms of an increase in charge in going from the ground state to the transition state with a consequent ordering of solvent molecules around the incipient ions.<sup>21</sup> The large negative entropies for the direct bimolecular displacement

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TABLE V<sup>a</sup>RATE CONSTANTS  $k_2$  ( $M^{-1} \text{SEC}^{-1}$ ) AT 30 AND 45° AND ACTIVATION PARAMETERS FOR THE REACTION

Entering group	Temp, °C	$10^3 k_2$ , $M^{-1} \text{sec}^{-1}$	$\Delta H_2^*$ , kcal/mol	$\Delta S_2^*$ , eu
Methanol Solvent				
CN <sup>-</sup>	30	8.49	7.5	-43.2
	45	15.34		
SeCN <sup>-</sup>	30	14.20	11.5	-29.1
	45	35.05		
SC(NH <sub>2</sub> ) <sub>2</sub>	30	49.40	8.2	-37.6
	45	94.00		
Dimethyl Sulfoxide Solvent				
I <sup>-</sup>	30	0.022		
	45	0.092		
SCN <sup>-</sup>	30	0.10	10.2	-43.3
	45	0.23		
SeCN <sup>-</sup>	30	0.81	10.3	-38.8
	45	1.82		
SC(NH <sub>2</sub> ) <sub>2</sub>	30	9.52	11.2	-31.0
	45	22.90		

<sup>a</sup> The rate constants  $k_2$  ( $M^{-1} \text{sec}^{-1}$ ) have been calculated by using the least-squares method.

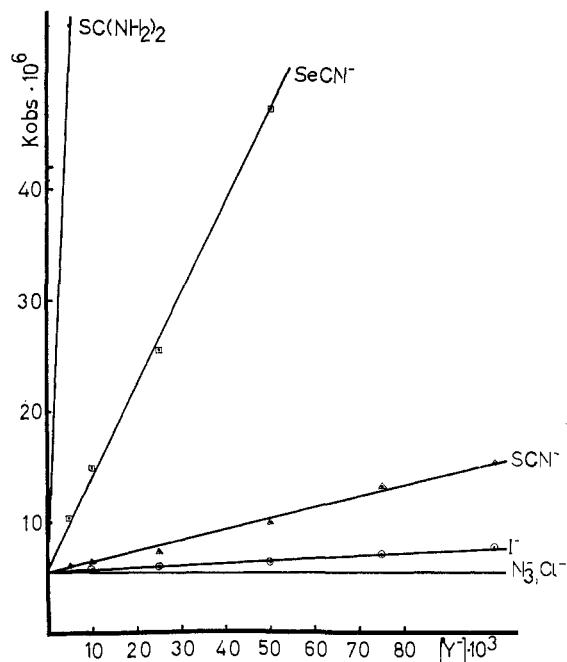


Figure 2.—Plot of  $k_{\text{obsd}}$  vs. reagent concentration for reactions of  $\text{trans-Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2(\text{ms})\text{Cl}$  with various nucleophiles in dimethyl sulfoxide at 30°.

are in agreement with the hypothesis of a net increase in bonding for an ordered and charged transition state.<sup>22</sup> Moreover, the formation of the activated complex from this hindered substrate requires particular stereochemical orientation for both the entering and the leaving groups.

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