

## Steric Effects and Activation Parameters in Nucleophilic Substitution Reactions of Platinum(II) Complexes

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The temperature dependence of the second-order rate constants for the replacement of  $X$  in  $trans$ -[Pt(PEt<sub>3</sub>)<sub>2</sub>(R)X]<sup>n+</sup>, (R = phenyl, *o*-tolyl, and mesityl) by a series of pyridine derivatives (X = CH<sub>3</sub>OH,  $n = 1$ ) and a series of thiourea derivatives (X = Cl,  $n = 0$ ) has been studied in methanol. The increase in steric hindrance, whether from methyl groups ortho to the donor atom in the trans ligand or ortho to the attacking atom in the entering nucleophile, leads to a reduction in rate and an increase in  $\Delta H^\ddagger$ , which, in most cases, is almost compensated by a large increase in  $\Delta S^\ddagger$ .

The effects are discussed in terms of solvation changes in the transition state.

### Introduction

The extensive study of the mechanisms of the substitution reactions of four-coordinate planar complexes of d<sup>8</sup> metal ions has revealed a consistent and generally obeyed pattern of behaviour.<sup>1,2,3</sup>

Interest is now turning to a much more detailed examination of the intimate mechanisms, the search for anomalies, and a fuller understanding of the role of the solvent, not only in the nucleophile independent pathways but also in a more general way. The use of bulky ligands in order to see the effect, on the rate of reaction, of steric hindrance of an associative mechanism was pioneered by Basolo<sup>4,5,6</sup> and has since been used extensively by many other investigators. Much of the work has been carried out at a single temperature and there is very little information about the relationship between steric effects and the activation parameters of the reaction. The major part of the published work consists of studies of the temperature dependence of the rate of displacement of Br<sup>-</sup> from [Pt(dien)Br]<sup>+</sup> by amines,<sup>7</sup> the exchange of thiocyanate in [Pt(AA)(SCN)<sub>2</sub>], where AA is a chelating diamine<sup>8,9</sup> and its displacement by thiourea,<sup>10</sup> but there are few other systematic studies. In this paper we report the temperature dependence of the rate of reaction of  $trans$ -[Pt(PEt<sub>3</sub>)<sub>2</sub>(R)X] (R = phenyl, *o*-tolyl, or mesityl) with

substituted pyridines (X = CH<sub>3</sub>OH) and with *N*-substituted thioureas (X = Cl) in methanol.

### Experimental

#### Materials

The complexes,  $trans$ -[Pt(PEt<sub>3</sub>)<sub>2</sub>RX] (R = phenyl, *o*-tolyl, or mesityl; X = Cl or NO<sub>3</sub>) were prepared by standard methods<sup>6,11</sup> and characterised by elemental analysis and infra-red spectroscopy. The substituted pyridines were purified by distillation from solid KOH in an atmosphere of nitrogen. All other chemicals were reagent grade. The methanol was dried by refluxing over Mg(OCH<sub>3</sub>)<sub>2</sub> and distilled.

#### Kinetics

The reactions were followed spectrophotometrically with an Optica CF4R Double Beam Recording Spectrophotometer. Solutions of known concentration of complex and the appropriate nucleophile were separately brought to the reaction temperature and the reaction was started by mixing the appropriate volumes of reactant solutions in the spectrophotometer cell which was then placed in the thermostatted compartment of the spectrophotometer. In the slower reactions, the spectra were scanned in the near ultra-violet from time to time and the presence of well defined isosbestic points throughout the reaction indicated the presence of only two absorbing species, the initial complex changing to the appropriate  $trans$ -[Pt(PEt<sub>3</sub>)<sub>2</sub>(R)Y] product. The final spectrum was generally identical to that of an independently prepared and characterised specimen of the postulated reaction product. The faster reactions were followed at a single wavelength with the recorder bed moving at a fixed speed. In all cases, sufficient nucleophile was present to ensure first-order kinetics and the plots of log<sub>10</sub>(A<sub>∞</sub> - A<sub>t</sub>) against time (A<sub>t</sub> and A<sub>∞</sub> being the absorbances at time  $t$  and at the end of the reaction respectively) were linear for at least three half lives. The pseudo first-order rate constants,  $k_{obs}$ , were obtained from the slopes of these

lines. For each substrate the reaction was studied at six different nucleophile concentrations.

## Results

The reactions of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>(R)Cl] with the strong nucleophile thiourea, and its *N*-substituted derivatives, follow the normal two term rate law,  $k_{\text{obs}} = k_1 + k_2[\text{tu}]$  and the plots of  $k_{\text{obs}}$  against the

concentration of nucleophile are linear and pass close to the origin, indicating that the  $k_1$  pathway makes a negligible contribution to these reactions. The second-order rate constants,  $k_2$ , obtained from the slope of these plots, are collected in Table I. Most other nucleophiles do not produce a second-order term on reaction with the chloro complex, the reaction going by way of the solvolytic path,<sup>12,13,14</sup> and so, in order to obtain second-order rate constants for amine entry, so as to examine the effect of placing methyl groups *ortho* to

TABLE I. Second-order Rate Constants for the Reaction: *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>(R)X] + Y = *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>(R)Y] + X<sup>a</sup> in Methanol.

R	X	Y	Temp. (°)	$k_2 \text{ M}^{-1} \text{ s}^{-1}$
phenyl	MeOH	pyridine	15.0	3.57
phenyl	MeOH	pyridine	20.0	4.95
phenyl	MeOH	pyridine	25.0	6.75
phenyl	MeOH	pyridine	30.0	9.00
phenyl	MeOH	pyridine	35.0	12.1
phenyl	MeOH	2-Me-py	20.0	0.049
phenyl	MeOH	2-Me-py	25.0	0.078
phenyl	MeOH	2-Me-py	30.0	0.140
phenyl	MeOH	2-Me-py	35.0	0.186
phenyl	MeOH	2-Me-py	40.0	0.266
<i>o</i> -tolyl	MeOH	pyridine	20.0	0.98
<i>o</i> -tolyl	MeOH	pyridine	25.0	1.21
<i>o</i> -tolyl	MeOH	pyridine	30.0	1.86
<i>o</i> -tolyl	MeOH	pyridine	35.0	2.49
<i>o</i> -tolyl	MeOH	pyridine	40.0	3.44
<i>o</i> -tolyl	MeOH	3-Me-py	20.0	1.26
<i>o</i> -tolyl	MeOH	3-Me-py	30.0	2.34
<i>o</i> -tolyl	MeOH	3-Me-py	40.0	4.25
<i>o</i> -tolyl	MeOH	4-Me-py	20.0	1.29
<i>o</i> -tolyl	MeOH	4-Me-py	30.0	2.25
<i>o</i> -tolyl	MeOH	4-Me-py	40.0	4.25
<i>o</i> -tolyl	MeOH	3,5-diMe-py	20.0	1.24
<i>o</i> -tolyl	MeOH	3,5-diMe-py	30.0	2.43
<i>o</i> -tolyl	MeOH	3,5-diMe-py	40.0	4.10
<i>o</i> -tolyl	MeOH	2-Me-py	20.0	0.012
<i>o</i> -tolyl	MeOH	2-Me-py	30.0	0.033
<i>o</i> -tolyl	MeOH	2-Me-py	35.0	0.049
<i>o</i> -tolyl	MeOH	2-Me-py	40.0	0.084
<i>o</i> -tolyl	MeOH	2,4-diMe-py	20.0	0.018
<i>o</i> -tolyl	MeOH	2,4-diMe-py	30.0	0.045
<i>o</i> -tolyl	MeOH	2,4-diMe-py	40.0	0.120
<i>o</i> -tolyl	MeOH	2,5-diMe-py	20.0	0.019
<i>o</i> -tolyl	MeOH	2,5-diMe-py	30.0	0.044
<i>o</i> -tolyl	MeOH	2,5-diMe-py	40.0	0.110
mesityl	MeOH	pyridine	20.0	0.16
mesityl	MeOH	pyridine	25.0	0.25
mesityl	MeOH	pyridine	30.0	0.35
mesityl	MeOH	pyridine	35.0	0.58
mesityl	MeOH	pyridine	40.0	0.85
mesityl	MeOH	2-Me-py	20.0	0.017
mesityl	MeOH	2-Me-py	25.0	0.032
mesityl	MeOH	2-Me-py	30.0	0.060
mesityl	MeOH	2-Me-py	35.0	0.128

TABLE I. (Cont.)

R	X	Y	Temp. (°)	$k_2 M^{-1} s^{-1}$
mesityl	MeOH	2-Me-py	40.0	0.231
phenyl	Cl	thiourea	20.0	4.15
phenyl	Cl	thiourea	25.0	5.00
phenyl	Cl	thiourea	30.0	6.3
phenyl	Cl	<i>N</i> -Me-thiourea	15.0	2.62
phenyl	Cl	<i>N</i> -Me-thiourea	30.0	5.00
phenyl	Cl	<i>N</i> -Me-thiourea	40.0	6.8
phenyl	Cl	<i>NN'</i> -diMe-thiourea	20.0	1.87
phenyl	Cl	<i>NN'</i> -diMe-thiourea	30.0	2.75
phenyl	Cl	<i>NN'</i> -diMe-thiourea	40.0	4.05
<i>o</i> -tolyl	Cl	thiourea <sup>b</sup>	30.0	0.65
<i>o</i> -tolyl	Cl	thiourea <sup>b</sup>	45.0	1.03
<i>o</i> -tolyl	Cl	<i>N</i> -Me-thiourea	20.0	0.45
<i>o</i> -tolyl	Cl	<i>N</i> -Me-thiourea	30.0	0.70
<i>o</i> -tolyl	Cl	<i>N</i> -Me-thiourea	40.0	1.09
<i>o</i> -tolyl	Cl	<i>NN'</i> -diMe-thiourea	20.0	0.27
<i>o</i> -tolyl	Cl	<i>NN'</i> -diMe-thiourea	30.0	0.44
<i>o</i> -tolyl	Cl	<i>NN'</i> -diMe-thiourea	40.0	0.73
mesityl	Cl	thiourea <sup>c</sup>	30.0	0.049
mesityl	Cl	thiourea <sup>c</sup>	45.0	0.094
mesityl	Cl	<i>N</i> -Me-thiourea	20.0	0.031
mesityl	Cl	<i>N</i> -Me-thiourea	30.0	0.060
mesityl	Cl	<i>N</i> -Me-thiourea	40.0	0.108
mesityl	Cl	<i>NN'</i> -diMe-thiourea	20.0	0.024
mesityl	Cl	<i>NN'</i> -diMe-thiourea	30.0	0.044
mesityl	Cl	<i>NN'</i> -diMe-thiourea	40.0	0.079

<sup>a</sup> Charges omitted to avoid confusion. <sup>b</sup> Data from Ref. 14. <sup>c</sup> Data from Ref. 13.

TABLE II. Rate Constants, Activation Enthalpies and Activation Entropies for the Reactions:  $trans-[Pt(PEt_3)_2(R)(X)] + Y \rightarrow trans-[Pt(PEt_3)_2(R)(Y)] + X^a$  in Methanol at 30.0°C.

R	X	Y	$k_2(30^\circ C)$ $M^{-1} s^{-1}$	$\Delta H^\ddagger$ kcal/mol	$\Delta S^\ddagger$ cal deg <sup>-1</sup> mol <sup>-1</sup>
phenyl	MeOH	pyridine	9.0	10.1 ± 0.1	-20.2 ± 0.2
phenyl	MeOH	2-Me-py	0.140	14.9 ± 1.0	-13.4 ± 3.0
<i>o</i> -tolyl	MeOH	pyridine	1.86	11.2 ± 0.7	-20.7 ± 2.2
<i>o</i> -tolyl	MeOH	3-Me-py	2.34	10.5 ± 0.1	-22.4 ± 0.3
<i>o</i> -tolyl	MeOH	4-Me-py	2.25	10.6 ± 0.7	-22.0 ± 2.3
<i>o</i> -tolyl	MeOH	3,5-diMe-py	2.43	10.3 ± 0.6	-22.9 ± 1.9
<i>o</i> -tolyl	MeOH	2-Me-py	0.033	17.1 ± 0.6	-9.0 ± 1.8
<i>o</i> -tolyl	MeOH	2,4-diMe-py	0.045	16.5 ± 0.7	-11.6 ± 2.1
<i>o</i> -tolyl	MeOH	2,5-diMe-py	0.044	15.4 ± 0.7	-15.4 ± 2.3
mesityl	MeOH	pyridine	0.355	14.8 ± 0.5	-12.0 ± 1.5
mesityl	MeOH	2-Me-py	0.060	23.5 ± 0.6	+13.4 ± 0.6
phenyl	Cl	thiourea	6.30	6.8 ± 0.5	-32.7 ± 1.7
phenyl	Cl	<i>N</i> -Me-thiourea	5.00	6.3 ± 0.4	-34.0 ± 1.5
phenyl	Cl	<i>NN'</i> -diMe-tu	2.75	6.4 ± 0.3	-35.5 ± 0.9
<i>o</i> -tolyl	Cl	thiourea	0.63	5.8	-40.5
<i>o</i> -tolyl	Cl	<i>N</i> -Me-thiourea	0.71	6.9 ± 0.3	-36.8 ± 0.9
<i>o</i> -tolyl	Cl	<i>NN'</i> -diMe-tu	0.44	8.5 ± 0.3	-32.4 ± 0.9
mesityl	Cl	thiourea	0.049	7.6	-39.6
mesityl	Cl	<i>N</i> -Me-thiourea	0.060	10.8 ± 0.2	-28.7 ± 0.8
mesityl	Cl	<i>NN'</i> -diMe-tu	0.044	10.5 ± 0.1	-30.3 ± 0.2

<sup>a</sup> Charges omitted to avoid confusion.

the nitrogen donor, it was necessary to use *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>(R)NO<sub>3</sub>] as the substrate. Molecular weight and conductivity data have shown unambiguously that this complex is almost completely dissociated in methanol<sup>12</sup> and so the observed reaction is the displacement of coordinated methanol by pyridine and its substituted derivatives. The plots of  $k_{\text{obs}}$  against [amine] were linear over the whole of the concentration range studied and all passed through the origin. The second-order rate constants, obtained from these plots, are also collected in Table I. The  $\log(k_2/T)$  was plotted against  $1/T$  in order to obtain the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values for the reactions. Good straight lines were obtained in all cases. The activation data are collected in Table II.

## Discussion

The factors that have been varied in studying the effect of increasing steric congestion in the transition state are, (i) methyl substitution in a position *ortho* to the carbon that is coordinated to the platinum in the substrate, (ii) methyl substitution *ortho* to the donor nitrogen in the entering heterocyclic amine and, (iii), methyl substitution on the nitrogens of the thiourea ligands. In addition, it should be pointed out that the triethylphosphine ligands are also extremely bulky and that the least congested of the complexes studied is nearly as crowded as the so-called "pseudo octahedral complexes" of the type, [Pt(Et<sub>4</sub>dien)X]<sup>+</sup> (Et<sub>4</sub>dien = *NNN'*-tetraethyl-1,5-diamino-3-azapentane). One may indeed wonder as to what extent the low intrinsic reactivity of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] is due to steric hindrance of the associative reaction. The steric congestion produced by changes of type (i) should not have an enormous effect on the rate of reaction because the steric hindrance is mainly the consequence of interactions between the methyl substituents and the ethyl groups on the phosphorus and should be present in the ground state as well as in the transition state.<sup>15</sup> The main kinetic effect from this type of hindrance occurs when the aryl ligand is *cis* to the leaving group and therefore takes up an axial position in the trigonal bipyramidal transition state. The great increase in congestion is seen in the very great decrease of reactivity and this study has been cited as evidence for the trigonal bipyramidal geometry of the transition state.<sup>6</sup>

Hindrance of type (ii) has been extensively studied by Cattalini who showed that the effects of *ortho* substitution were additive and varied from a rate increase factor of 10 to 300 per methyl group depending upon the nature of the reaction.<sup>16-22</sup>

Although, geometrically, the methyl groups from the substituted pyridine take up symmetrically equivalent positions to those from the phenyl substituent (*i.e.*, both ligands occupy equatorial positions in the trigonal bipyramidal transition state) there is a *net* increase

of congestion with respect to the ground state, where the amine is not present, and this should be reflected in the kinetics.

The variation in the extent of *N*-methyl substitution in the thiourea is sufficiently remote from the reaction centre (assuming that coordination is through the sulfur) for there to be little or no effect on the congestion there and this is apparent in the lack of significant variation of the rate constants in Table I.

In general terms, the effect of the structural changes on the rate of reaction is in the direction that might be predicted knowing that the mechanism is associative. If the rate constants at 30.0°C are compared it will be seen that, with the weak nucleophile, pyridine, replacing the weakly bonded methanol, there is a decrease in reactivity on increasing the extent of *ortho* methyl substitution in the bound phenyl group in the ratio 25:5.2:1 for the change phenyl:*o*-tolyl:mesityl. When the strong nucleophile, thiourea, replaces the more strongly bonded chloride, the effect is heightened and the corresponding ratios become 129:13:1 and one could possibly argue that the transition state for a strong nucleophile and a well bound leaving group tends to be more compact and hence more sensitive to steric hindrance; but the difference is not great if considered in terms of energy differences. With 2-methylpyridine replacing methanol, the sequence of reactivity changes and the ratios become, 2.3:0.55:1 and an inspection of Table I will show that the ratio and even the sequence of reactivity will depend upon the temperature chosen for the comparison.<sup>23</sup> Observations of this sort always present a dilemma when a systematic variation of a property of the reagents or the solvent leads to relatively small changes in the rates of reaction (when expressed as free energies of activation) but large variations in the enthalpies and entropies of activation.

In principle, one ought to be able to predict, in qualitative terms, the nature of the changes expected in the enthalpy and entropy of activation as a result of an increase in steric hindrance. It is reasonably self-evident that, in an associative process where bond making is important in the transition state, the enthalpy of activation should increase as a result of the greater repulsive interactions encountered in achieving the optimum bonding separations. A simple minded view would also predict that this hindrance would reduce the number of possible ways of arranging the atoms and energy levels in the transition state and thereby lead to a decrease in the entropy of activation. Ingold<sup>24</sup> has pointed out that a somewhat more sophisticated approach is required which should take into account the shape of the potential surface associated with the reaction and even the mass of the substituents, but the combined contributions lead to a decrease in the entropy of activation as the steric hindrance is increased in the displacement of chloride or bromide from tetrahedral

carbon by halide ions in the Finkelstein reaction. Of course, arguments of this sort are only valid when the reaction is carried out in the gas phase or when solvent effects are only of minor importance.

Examination of the data in Table II shows quite clearly that the variation of the free energy of activation (which should be proportional to the logarithm of the rate constant) is far less than the variations in the entropies and enthalpies of activation. The data relating to the entry of thioureas, if taken in isolation, might well fit into the simplified picture in which there is an increase in the  $\Delta H^\ddagger$  value as a result of placing methyl groups in the *ortho* positions of the phenyl substituent and the  $\Delta S^\ddagger$  values do not vary greatly, or systematically and remain large and negative, in the  $-30$  to  $-40$  cal deg $^{-1}$ mol $^{-1}$  region, as might be expected for an associative process where charge separation develops in the transition state. However, increase in steric hindrance when methanol is the leaving group, whether this comes from methyl substitution in the entering nucleophile or in the *trans* ligand, is accompanied by an increase (sometimes quite dramatic) in  $\Delta H^\ddagger$  but this is generally accompanied by a large, and almost compensating, increase in  $\Delta S^\ddagger$ . If the values of  $\Delta H^\ddagger$  are plotted against those of  $\Delta S^\ddagger$ , Figure 1, a roughly linear relationship is observed (slope = 350°K) and the line is straddled by the data for the reaction of the chloro complexes with the thioureas. This is a fairly typical manifestation of the so-called "Compensation Law".<sup>25</sup> It is generally believed that relationships of this sort are common for processes where the activation parameters are dominated by solvation changes,<sup>26</sup> since the processes involving the transfer of solvent molecules between the strongly ordered region adjacent to the metal complex, the highly disordered region outside and the relatively ordered region

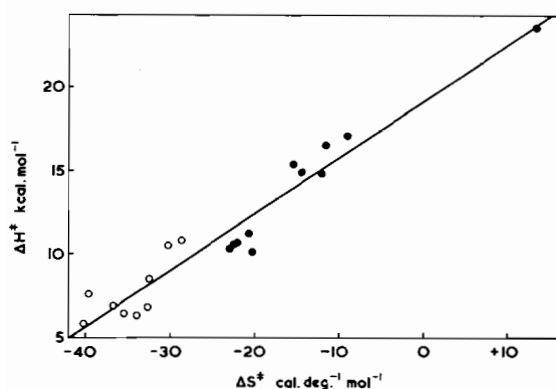


Figure 1. Plot of  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$  for (i) the displacement of MeOH from  $trans$ -[Pt(PEt $_3$ ) $_2$ (R)MeOH] $^+$  by pyridine and its methyl substituted derivatives, ● and (ii) the displacement of Cl $^-$  from  $trans$ -[Pt(PEt $_3$ ) $_2$ (R)Cl] by thiourea and its *N*-methyl derivatives, ○ in methanol (R = phenyl, *o*-tolyl, or mesityl).

of the "bulk solvent" are associated with small values of  $\Delta G^\ddagger$  although the associated  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values are quite considerable. Ives and Marsden<sup>27</sup> have discussed this at length in connection with the effect of alkyl substitution on the enthalpy and entropy of ionisation and the concept of "internal changes" relating to bonding changes in the substrates, associated with significant  $\Delta G^\ddagger$  values and "external changes" relating to solvation changes with  $\Delta G^\ddagger$  ideally zero and  $\Delta H^\ddagger = T\Delta S^\ddagger$ , could well be applied to transition states and activation parameters. The large, negative  $\Delta S^\ddagger$  values for the reactions in which the neutral chloro complexes react with the neutral thiourea are consistent with the transfer of solvent molecules to the highly ordered region in the vicinity of the activated complex as a result of the developing charge. The replacement of coordinated methanol, on the other hand, has many features in common with the complex formation reactions of solvated metal ions, where it is not possible to distinguish between dissociatively or associatively activated substitution processes without knowing the rate of solvent exchange and the concentration range over which the rate law is first-order with respect to the entering nucleophile. In the absence of data for methanol exchange in the  $trans$ -[Pt(PEt $_3$ ) $_2$ (R)(MeOH)] $^+$  complexes, it is not possible to say whether the derived second-order rate constant is truly associated with a bimolecular process or whether it is a composite term of the type  $k_2 = k_a k_b / k_c [\text{MeOH}]$ , where  $k_a$  is the rate constant for the dissociation of the methanol and  $k_b$  and  $k_c$  are the rate constants for the capture of the intermediate by the nucleophile, Y, under study and by solvent methanol, respectively (the simple kinetics are only observed if  $k_c [\text{MeOH}] \gg k_b [\text{Y}]$ ), resulting from a D mechanism. Dissociative, I $_d$ , or associative, I $_a$ , interchange would also produce a simple second-order kinetic form if the pre-formed aggregate was only present in small concentrations.

The large  $\Delta H^\ddagger$  and positive  $\Delta S^\ddagger$  associated with the reaction of  $trans$ -[Pt(PEt $_3$ ) $_2$ (mesityl)MeOH] $^+$  with 2-methyl-pyridine might be due to a sterically induced discharge of solvent molecules from the hydrocarbon like exterior of the activated complex into the disordered region and bulk solvent but, until the methanol exchange rates are known, a change towards a dissociatively activated process cannot be ruled out.

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