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Reactivity studies of *trans*-[PtClMe(SMe$_2$)$_2$] towards anionic and neutral ligand substitution processes

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Abstract

Reaction of *trans*-[PtClMe(SMe$_2$)$_2$] with the mono anionic ligands azide, bromide, cyanide, iodide and thiocyanate result in substitution of the chloro ligand as the first step. In contrast the neutral ligands pyridine, 4-Me-pyridine and thiourea substitute a SMe$_2$ ligand in the first step as confirmed by ^{1}H NMR spectroscopy and the kinetic data. Detailed kinetic studies were performed in methanol as solvent by use of conventional stopped-flow spectrophotometry. All processes follow the usual two-term rate law for square-planar substitutions, $k_{obs} = k_1 + k_2[Y]$ (where $k_1 = k_{MeOH}[MeOH]$), with $k_1 = 0.088 \pm 0.004\ s^{-1}$ and $k_2 = 1.18 \pm 0.13$, 3.8 ± 0.3, 17.8 ± 1.3, 34.9 ± 1.4, $75.3 \pm 1.1\ mol^{-1}\ dm^3\ s^{-1}$ for $Y^- = N_3$, Br, CN, I and SCN respectively at 298 K. The reactions with the neutral ligands proceed without an appreciable intercept with $k_2 = 5.1 \pm 0.3$, 15.3 ± 1.8 and $195 \pm 3\ mol^{-1}\ dm^3\ s^{-1}$ for Y = pyridine, 4-Me-pyridine and thiourea, respectively, at 298 K. Activation parameters for MeOH, N_3^-, Br^-, CN^-, I^-, SCN^-, and Tu are $\Delta H^{\neq} = 47.1 \pm 1.6$, 49.8 ± 0.6, 39 ± 3, 32 ± 8, 39 ± 5, 34 ± 4 and $31 \pm 3\ kJ\ mol^{-1}$ and $\Delta S^{\neq} = -107 \pm 5$, -77 ± 2, -104 ± 9,-113 ± 28, -85 ± 18, -94 ± 14 and $-97 \pm 10\ J\ K^{-1}\ mol^{-1}$, respectively. Recalculation of k_1 to second-order units gives the following sequence of nucleophilicity: MeOH < N_3^- < Br^- ~ py < 4 − Me − py ~ CN^- < I^- < SCN^- < Tu (1:13:42:57:170:200:390:840:2170) at 298 K. Variation of the leaving group in the reaction between *trans*-[PtXMe(SMe$_2$)$_2$] and SCN^- follows the same rate law as stated above with $k_2 = 75.3 \pm 1.1$, 236 ± 4 and $442 \pm 5\ mol^{-1}\ dm^3\ s^{-1}$ for $X^- = Cl$, I and N_3, respectively, at 298 K. The corresponding activation parameters were determined as $\Delta H^{\neq} = 34 \pm 4$, 32 ± 2 and $39.3 \pm 1.7\ kJ\ mol^{-1}$ and $\Delta S^{\neq} = -94 \pm 14$, -86 ± 8 and $-68 \pm 6\ J\ K^{-1}\ mol^{-1}$. All the kinetic measurements indicate the usual associate mode of activation for square planar substitution reactions as supported by large negative entropies of activation, a significant dependence of the reaction rate on different entering nucleophiles and a linear free energy relationship.

Keywords: Platinum; Kinetics; Substitution reactions; Mechanism

1. Introduction

Square planar substitution reaction at Pt(II) centres have been extensively studied and contributed significantly to our current understanding of ligand effects and reaction mechanisms. Several groups contributed in this area to systematically investigate the effects of the *cis* and *trans* directing ligand, the leaving group and the entering nucleophiles on the reactivity of the complexes and resulting reaction mechanisms [1].

Although complexes containing platinum(IV)—carbon σ-bonds were first reported almost a century ago [2] it was not until 1957 that the first complexes containing platinum(II)—carbon σ-bonds were prepared [3]. These first complexes were restricted to those containing metal—carbon bonds from bidentate ligand systems and it was only in 1959 that complexes containing platinum(II)—methyl σ-bonds were reported [4].

The synthesis of sulphide complexes of platinum(II) containing σ-carbon ligands was since well established [5] and have been used to demonstrate dissociative substitution processes [6] on square planar complexes. It is well known [7] that ligand substitution processes *trans* to a σ-carbon atom are extremely rapid due to the high *trans*

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effect of these ligands. In addition to the large *trans* effect of σ-carbon ligands it is also well known that these ligands exert an appreciable *trans* influence by weakening the metal—ligand bond opposite of itself. In this regard it was of interest to us to investigate systems containing a σ-carbon *trans* directing ligand and electron donating thioether ligands in the *cis* positions in a kinetic study. Details of our findings in a comprehensive study on the reactivity and substitution patterns in *trans*-[PtXMe(SMe_2)$_2$] (X^- = Cl, I, N_3) complexes towards both anionic and neutral nucleophiles are reported in this paper.

2. Experimental

2.1. Chemicals

Methanol of analytical grade (Riedel-de Haën) was freshly distilled from CaH_2 under dinitrogen prior to use. K_2PtCl_4 (Next Chimica) was used as received. Analytically pure SMe_2 (Merck), MeLi (Aldrich), NaN_3 (Merck), LiBr (Merck), NaI (Merck), NaSCN (Mallinckrodt), KCN (Merck), pyridine (Merck), 4-Me-pyridine (Merck) and thiourea (Merck) were used as received. All moisture and oxygen sensitive procedures were performed using standard anaerobic techniques.

2.2. Preparation of complexes

[PtClMe(COD)] was prepared according to established procedures [8]. ^{1}H NMR (CD_3OD): 0.80 (t, 3H, Me, $^2J_{Pt-H} = 71.8$ Hz), 2.25–2.60 (m, 8H, $4 \times CH_2$), 4.55 (t, 2H, CH=CH *trans* to Cl, $^{2.5}J_{Pt-H} = 77.0$ Hz), 5.43 (t, 2H, CH=CH *trans* to Me, $^{2.5}J_{Pt-H} = 36.2$ Hz).

cis-and trans-[PtCl$_2$(SMe$_2$)$_2$]: The original procedure of Cox et al. [9] was modified as follows: K_2PtCl_4 (1.00 g, 2.41 mmol) was dissolved in 40 cm^3 of cold water and SMe_2 (1.0 mL, 0.846 g, 13.62 mmol) was added with vigorous stirring. A pink suspension indicative of the Magnus salt [Pt(SMe_2)$_4$][$PtCl_4$] was rapidly formed. The reaction mixture was heated to 80 °C upon which time it had turned yellow indicative of conversion to a mixture of *cis*- and *trans*-[$PtCl_2(SMe_2)_2$]. The solution was left to cool to room temperature and was subsequently extracted with dichloromethane until colourless. The dichloromethane fractions were combined, dried over anhydrous $MgSO_4$, filtered and evaporated to dryness to obtain the desired product in excellent yields (0.902 mg, 96%). ^{1}H NMR (CD_3OD): *cis*-[$PtCl_2(SMe_2)_2$]: 2.55 (t, $^3J_{Pt-H} = 49.8$ Hz); *trans*-[$PtCl_2(SMe_2)_2$]: 2.43 (t, $^3J_{Pt-H} = 41.1$ Hz).

trans-[PtClMe(SMe$_2$)$_2$]: Initially *trans*-[PtClMe(SMe_2)$_2$] was prepared by the action of MeLi on a mixture of *cis*- and *trans*-[$PtCl_2(SMe_2)_2$] as described by Puddephatt and co-workers [10]. ^{1}H NMR ($CDCl_3$): 0.52 (t, 3H, Me, $^2J_{Pt-H} = 79.2$ Hz); 2.57 (t, 12H, $2 \times SMe_2$, $^3J_{Pt-H} = 41.1$ Hz); (CD_3OD): 0.54 (t, 3H, Me, $^2J_{Pt-H} = 80.6$ Hz); 2.53 (t, 12H, $2 \times SMe_2$, $^3J_{Pt-H} = 54.2$ Hz).

Alternatively *trans*-[PtClMe(SMe_2)$_2$] was also synthesised from [PtClMe(COD)] as follows: [PtClMe(COD)] (106 mg, 0.30 mmol) was dissolved in a mixture of methanol (4 mL) and SMe_2 (1.5 mL) and stirred overnight at room temperature. All volatile components were removed under reduced pressure; methanol (3 mL) was added and again removed under reduced pressure. ^{1}H NMR spectroscopic analysis confirmed quantitative conversion to the desired complex. Solutions of **1** prepared in this way were found to be of sufficient purity for further investigation.

*trans-[PtIMe(SMe$_2$)$_2$] (**2**):* Prepared in situ by the addition of NaI (150 mg, 1.0 mmol) to the solution of **1** (1.0 mM, 250 mL) destined for the kinetic investigation. ^{1}H NMR analysis of a 10 mM solution in CD_3OD prepared in a similar way were identical to that reported by Scott and Puddephatt [10]. ^{1}H NMR (CD_3OD): 0.71 (t, 3H, Me, $^2J_{Pt-H} = 77.0$ Hz); 2.61 (t, 12H, $2 \times SMe_2$, $^3J_{Pt-H} = 55.0$ Hz).

*trans-[PtN$_3$Me(SMe$_2$)$_2$] (**3**):* Prepared in situ by the addition of NaN_3 (98 mg, 1.5 mmol) to the solution of **1** (1.0 mM, 250 mL) destined for the kinetic investigation. ^{1}H NMR analysis of a 10 mM solution in CD_3OD prepared in a similar way verified the formation of the desired complex. ^{1}H NMR (CD_3OD): 0.69 (t, 3H, Me, $^2J_{Pt-H} = 72.8$ Hz); 2.54 (t, 12H, $2 \times SMe_2$, $^3J_{Pt-H} = 54.7$ Hz).

2.3. NMR measurements

^{1}H and NMR spectra were recorded at 295 K in CD_3OD on a Bruker 300 MHz spectrometer with chemical shifts reported in ppm and coupling constants in Hz. The ^{1}H spectra were calibrated on the residual CH_3OH peak at $\delta = 4.79$ or the $CHCl_3$ peak at 7.26 ppm as internal standards.

The substitution patterns were verified by ^{1}H NMR spectroscopy by using 10 mM solutions of **1** in CD_3OD and addition of the various nucleophiles. The experiments were performed in two steps with the first corresponding to the addition of slightly less than one equivalent of the nucleophile followed by addition of at least a 10 times excess of the nucleophile as the second step. Detailed results of the study are given as ESI.

2.4. Kinetic measurements

Methanol was selected as solvent for the kinetic investigation ensuring adequate solubility of all reagents used. UV–Vis spectra were recorded at 298 K on a Hitachi 150-20 spectrophotometer between 250 and 450 nm. Suitable wavelengths for the kinetic measurements were determined by mixing of a methanol solution of **1** with the respective ligands in a 1-cm quartz cell and comparing the resulting spectra with that of the spectra of the parent complex. The kinetic measurements were done on a modified Durrum D110 stopped flow spectrophotometer equipped with a water bath regulating the temperature to within 0.2 °C. The total concentration of platinum was

usually ca. 0.40 mmol dm^{-3} and nucleophile concentrations were always at least 10 times larger after mixing to ensure pseudo first-order reaction conditions. Selected reactions were investigated as a function of temperature between 288 and 309 K to enable the determination of activation parameters. The kinetic traces for all reactions investigated showed well-defined first-order behaviour. In the case of nucleophiles involved in consecutive reactions the rate difference between the first and second reactions were substantial enough to enable isolation and accurate analysis of the data for the first reaction. Data were collected and all observed pseudo first-order rate constants were determined using the OLIS program [11] for the data analysis. All least-squares fits were performed using SCIENTIST [12], the observed pseudo first-order rate constants were fitted against the ligand concentration using the linear model, typical for square planar substitution reactions, see Scheme 1. Activation parameters were calculated using the exponential form of the Eyring equation. All individual values for k_{MeOH} were used in the final calculation of the activation parameters for the solvent assisted pathway. Complete primary kinetic data are given as ESI.

3. Results and discussion

3.1. Synthesis

Initially compound **1** was prepared according to the method of Puddephatt [10] through the action of MeLi on a mixture of *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$ as substrate. Due to the limited stability of **1** it was later found more convenient to prepared bulk samples of [PtClMe(COD)] and by substituting the COD with SMe_2 to prepare fresh quantities of **1** as desired. In this regard the thioether substrates **2** and **3** were prepared in situ by the addition of a slight excess of NaI and NaN_3, respectively, to **1** to ensure complete substitution in these dilute solutions by the time the kinetic measurements were made. No adverse effects were observed in the subsequent studies with thiocyanate due to the presence of low quantities of iodide and azide, respectively.

3.2. Stoichiometry

Two distinctly different sets of kinetic behaviour were observed depending on the choice of the entering nucleophile. The substitution patterns were investigated using ^1H NMR and it was confirmed that free SMe_2 were observed in all reactions with neutral ligands. For the anionic ligands a shift in the methyl and SMe_2 resonances, before free SMe_2 is observed, confirmed substitution of the Cl^- ligand in the first step.

In the case of anionic nucleophiles (halides and pseudohalides) the reaction is expressed as in Eq. (1) where Y denotes the entering ligand:

$$trans\text{-}[PtClMe(SMe_2)_2] + Y^- \rightarrow trans\text{-}[PtYMe(SMe_2)_2] + Cl^- \quad (1)$$

For neutral ligands the reaction is defined by the following equation:

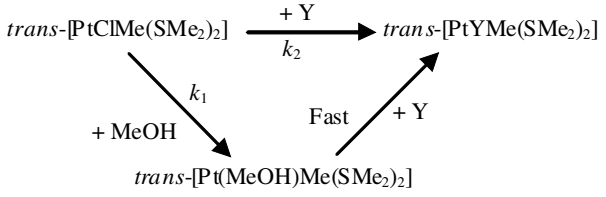
$$trans\text{-}[PtClMe(SMe_2)_2] + Y \rightarrow [PtClMe(SMe_2)Y] + SMe_2 \quad (2)$$

The effect of the entering nucleophile on the kinetic behaviour of **1** was investigated in methanol with N_3^-, Br^-, I^-, CN^- and SCN^- according to Eq. (1) and with pyridine, 4-Me-pyridine and thiourea according to Eq. (2).

Furthermore the effect of the leaving group, $X = Cl^-$, N_3^- and I^-, was evaluated in methanol according to Eq. (3), using thiocyanate as entering ligand:

$$trans\text{-}[PtXMe(SMe_2)_2] + SCN^- \rightarrow trans\text{-}[Pt(SCN)Me(SMe_2)_2] + X^- \quad (3)$$

The ^1H NMR studies on the halides and pseudo halides indicated consecutive reactions for N_3^-, CN^-, SCN^- while only single reactions were observed for Br^- and I^-. The ^1H NMR studies using the neutral ligand indicated displacement of a single SMe_2 by pyridine and 4-Me-pyridine under the conditions investigated while consecutive reactions were observed for thiourea. Due to the number of possible substitution reactions and resulting geometries the ^1H spectra tended to be very complex in nature and all reaction products could thus not be fully characterised. In this regard the presence of a free SMe_2 resonance was used as a qualitative indication of SMe_2 substitution and in combination with the kinetic behaviour it was clear that two distinctly different processes were operational. It has been reported previously by Wendt et al. [13] that strong neutral nucleophiles, such as phosphines, substitute the thioether ligands from a series of *trans*-[PtCl(aryl)(thioether)$_2$] complexes. Consecutive reactions were also observed with cyanide and thiocyanate which were interpreted as thioether substitution after the chloride has already been replaced. In addition the lability of the SMe_2 ligands towards substitution with other neutral π-ligands have been used to prepare a series of complexes of the general type *trans*-$[PtClMe(L)_2]$ ($L = PPh_3$, PPh_2Fc, $P(NMe_2)_3$, $AsPh_3$ and As(*p*-Me-Ph)$_3$) [14–17] from *trans*-$[PtClMe(SMe_2)_2]$ and analogous *trans*-$[PtClPh(L)_2]$ ($L = PPh_3$, PPh_2Fc, $AsPh_3$ and $SbPh_3$) complexes starting from *trans*-$[PtClPh(SMe_2)_2]$.



Scheme 1. Classical mechanism for square planar substitution showing both the direct partway (k_2) as well as the parallel solvent assisted pathway (k_1).

3.3. Kinetics and mechanism

Plots of observed rate constants vs. the concentration of the entering nucleophiles are given in Fig. 1a for the anionic ligands and in Fig. 1b for the neutral ligands, respectively.

The intercepts observed in Fig. 1a could in principle be a combination of a reversible process (equilibria) and a solvent assisted substitution pathway. The fact that the intercepts are the same within experimental error for the various anionic entering nucleophiles indicate that reversibility can be ruled out since the equilibria should be different for the different nucleophiles. Upon stoichiometric addition of ligand to the metal complex, complete conversion, as manifested by the NMR and UV/Vis results, was observed. Thus, the intercepts can be attributed to the contribution from a common solvent assisted pathway on the observed reaction rate as shown in Scheme 1 for the classic two-step square-planar substitution mechanism.

All reactions with the anionic ligands therefore proceed in accordance with the usual two-term rate law for square-planar substitution reactions as depicted in Scheme 1 and Eq. (4), where k_2 refers to the direct substitution process and k_1 to the solvent assisted pathway:

$$k_{obs} = k_1 + k_2[Y] \quad \text{with } k_1 = k_{MeOH}[MeOH] \tag{4}$$

The substitution behaviour of the neutral ligands, shown in Fig. 1b, all have an intercept close to zero indicating no significant solvent assisted pathway or reversibility to be operative even though classical square-planar substitution as proposed in Scheme 1 and Eq. (4), still prevails.

Second-order rate constants at 298 K for the reactions between **1** and the various nucleophiles and the corresponding activation parameters calculated from the Eyring plots in Fig. 2 are given in Table 1.

The order of reactivity based on the values of k_2 and k_{MeOH} in Table 1 is MeOH < N_3^- < Br^- ~ py < 4–Me-py ~ CN^- < I^- < SCN^- < Tu or in relative numbers normalised to MeOH ca. 1:13:42–55:170–200:390:840:2200. A significant dependence on the nature of the incoming nucleophile is evident.

Since earlier studies [18] indicated that the leaving group may have a significant effect on the rate of substitution this variable was investigated according to Eq. (3). Second-order rate constants and activation parameters for the reaction at 298 K are summarised in Table 2.

The order of reactivity towards thiocyanate, based on the values of k_2 in Table 2, is Cl^- < I^- < N_3^- or in relative numbers about 1:3:6. For the substitution of I^- and N_3^- reactivities comparable to the reaction between **1** and thiourea were encountered. The contribution of the solvent assisted pathway was negligible as compared to the fast direct substitution pathway. Furthermore, in accordance with an associative mode of activation, the effect of various leaving groups was small (6×) as compared to the effect of various entering nucleophiles (2000×) and only relevant in as much as it renders the metal centre more electrophilic.

Even though different substitution patterns were observed in the current study of **1** (Cl^- vs. SMe_2) the rate determining step in an associative mechanism would be

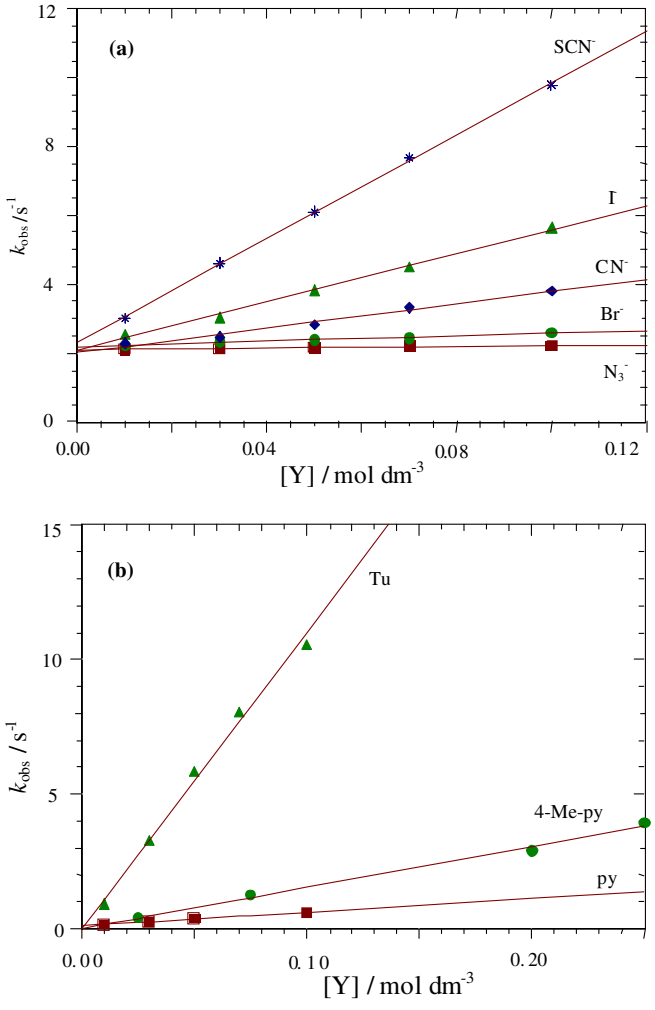


Fig. 1. Concentration dependence of k_{obs} at 298 K for reactions of **1** with (a) anionic ligands (b) neutral ligands.

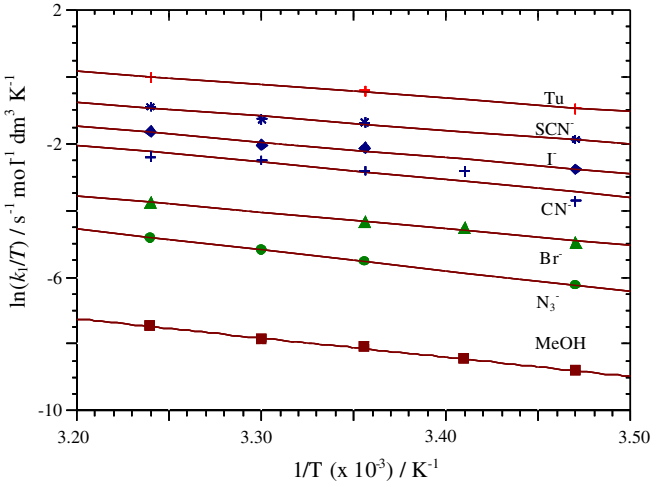


Fig. 2. Eyring plots for the reactions of all nucleophiles with **1**.

Table 1
Rate constants at 298 K and activation parameters for the reactions between **1** and nucleophiles, Y, in methanol

Y	k_2 (mol^{-1} dm^3 s^{-1})	$\Delta H_2^{\neq}$ (kJ mol^{-1})	$\Delta S_2^{\neq}$ (J K^{-1} mol^{-1})	k_1 (s^{-1})	k_{MeOH}[a] (mol^{-1} dm^3 s^{-1})	$\Delta H_{MeOH}^{\neq}$ (kJ mol^{-1})	$\Delta S_{MeOH}^{\neq}$ (J K^{-1} mol^{-1})
N_3^-	1.18(13)	49.8(6)	−77(2)	2.088(8)	0.0846(2)	48.5(18)	−103(6)
Br^-	3.8(3)	39(3)	−104(9)	2.180(18)	0.0883(8)	48.1(9)	−104(3)
I^-	34.9(14)	39(5)	−85(18)	2.08(8)	0.101(4)	40(6)	−129(20)
CN^-	17.8(13)	32(8)	−113(28)	2.00(8)	0.081(3)	52(3)	−90(8)
SCN^-	75.3(11)	34(4)	−94(14)	2.31(6)	0.094(3)	47(6)	−109(19)
py	5.1(3)	–	–	0	0	–	–
4-Me-py	15.3(18)	–	–	0	0	–	–
Tu	195(3)	31(3)	−97(10)	0	0	–	–

[a] $k_{MeOH} = k_1/[MeOH]$.

Table 2
Rate constants at 298 K and activation parameters for the reactions between *trans*-$[PtXMe(SMe_2)_2]$ and SCN^- in methanol

X	k_2 (mol^{-1} dm^3 s^{-1})	$\Delta H_2^{\neq}$ (kJ mol^{-1})	$\Delta S_2^{\neq}$ (J K^{-1} mol^{-1})	k_1 (s^{-1})	k_{MeOH} (mol^{-1} dm^3 s^{-1})	$\Delta H_{MeOH}^{\neq}$ (kJ mol^{-1})	$\Delta S_{MeOH}^{\neq}$ (J K^{-1} mol^{-1})
Cl^-	75.3(11)	34(4)	−94(14)	2.31(6)	0.094(3)	47(6)	−109(19)
I^-	236(4)	39.3(17)	−68(6)	0	0	–	–
N_3^-	442(5)	32(2)	−86(8)	0	0	–	–

the formation of the five coordinate intermediate incorporating the original four ligands as well as the entering nucleophile with the latter as the only variable. In support of this assignment a Linear Free Energy relationship [19] was constructed from the data in Table 1 at 298 K for the reaction between **1** and the various nucleophiles according to Eq. (5), see Fig. 3:

$$\ln(k_1) = s n^{\circ}_{Pt} \quad (5)$$

The nucleophilicity constant, n°_{Pt}, refers to the relative affinity [20] of platinum for various nucleophiles as determined experimentally during the reaction with *trans*-$[PtCl_2(pyridine)_2]$.

In general an excellent linear free energy relationship was found for the various substitution processes with the pyridine ligands and cyanide being the outliers (4-Me-pyridine was omitted from the LFER since no value for n°_{Pt} was available). The exact reason for this behaviour is not clearly understood at this point, but in the case of cyanide the lower than expected reactivity may be indicative of N-coordination *trans* to the σ-coordinated C atom of the methyl group. The slope of the line in Fig. 3 gave a value of 0.74 (*s* in Eq. (5) indicating **1** to be less discriminative towards different entering nucleophiles than the model substrate *trans*-$[PtCl_2(pyridine)_2]$ on which the values for n°_{Pt} are based.

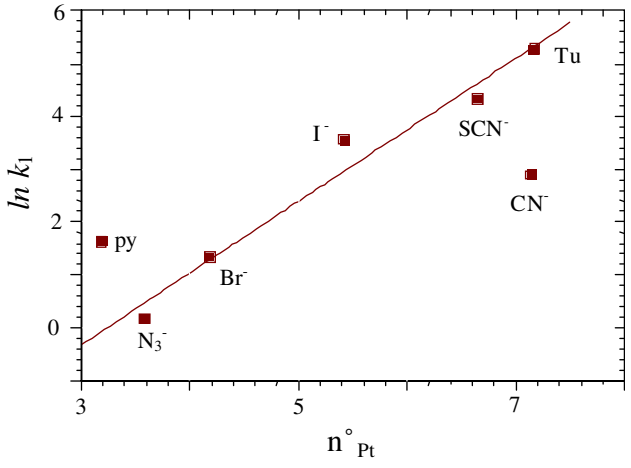


Fig. 3. Linear Free Energy relationship at 298 K for the reaction of **1** with both anionic and neutral entering nucleophiles vs. the nucleophilicity index, n°_{Pt}.

It is well known that the high *trans* effect of ligands such as CO and ethylene originates form its ability to stabilise the five coordinate intermediate through π back donation of the excess electron density. In this regard it was found that the $T\Delta S^{\neq}$ contributions for substitution reactions on Pt(II) olefin substrates contributed from 40% to 70% to the free energy of activation [21–24].

Table 3 gives a breakdown of the relative contribution of the activation parameters on the free energy of activation for the current study. The $T\Delta S^{\neq}$ contributions vary between 30% and 50% indicating the formation of the five coordinate intermediate to be less of an energetic driving force than in complex containing ligands capable of π back donation.

Comparison of the data obtained during this study with similar systems from the literature is presented in Table 4.

It is clear that the reaction rates of the substitution processes *trans* to methyl are only marginally larger than those obtained *trans* to phenyl and anisyl. The lower activity observed for the corresponding mesityl SMe_2 complex may be attributed to increased steric crowding of the metal centre by the 2,6 substituents of the mesityl ligand. The PEt_3 complexes are significantly less reactive than the corresponding S-donor ligands as a combined result of steric

Table 3
Activation parameter contributions to the free energy of activation, $T\Delta S^{\neq}$ calculated for **1**–**3** at 298 K

	1							**2**	**3**
	MeOH	N_3^-	Br^-	I^-	CN^-	SCN^-	Tu	SCN^-	SCN^-
$\Delta H^{\neq}$ (kJ mol^{-1})	47.1	49.8	39	39	32	34	31	39.3	32
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−107	−77	−104	−85	−113	−94	−97	−68	−86
$-T\Delta S^{\neq}$ (kJ mol^{-1})	31.9	22.9	31.0	25.3	33.7	28.0	28.9	20.3	25.6
$\Delta G^{\neq}$ (kJ mol^{-1})	79.0	72.7	70	64.3	65.7	62	59.9	59.6	57.6
% $T\Delta S^{\neq}$	40	31	44	39	51	45	48	34	44

Table 4
Rate constants for substitution of chloride *trans* to carbon (π-olefinic and σ alkyl/ aryl) with MeOH and I^- as nucleophiles at 298 K

Substrate	k_{MeOH} (mol^{-1} dm^3 s^{-1})	k_2 (mol^{-1} dm^3 s^{-1})	Reference
trans-[PtClPh(PEt_2)$_2$]	8.5×10^{-5}	0.06	[25]
trans-[PtClMe(PEt_2)$_2$]	4×10^{-4}	0.4	[25]
trans-[PtClPh(SEt_2)$_2$]	0.011	1.7	[13]
trans-[PtClPh(SMe_2)$_2$]	0.038	27.4	[13]
trans-[PtCl(mesityl)(SMe_2)$_2$]	0.022	8.1	[13]
trans-[PtCl(*p*-anisyl)(SMe_2)$_2$]	0.036	30.6	[13]
trans-[PtClMe(SMe_2)$_2$]	0.090	34.9	TW
[Pt(C_2H_4)Cl_3]$^-$	171	49400	[22]
[Pt(C_8H_{14})Cl_3]$^-$	76	5701	[22]

crowding and the Pt centre being less electrophilic and hence less susceptible to nucleophilic attack. The same argument holds true for replacement of SMe_2 by the more bulky SEt_3 ligand. The reactions *trans* to the π-accepting ethylene and cyclooctene ligands is significantly faster than all reactions *trans* to a σ-carbon. From the results presented in Tables 3 and 4 it is clear that the reactivity of square planar substitution processes following an associative mode of activation is significantly more influenced by stabilization of the five coordinate transition state (*trans* effect) than by ground state destabilization (*trans* influence).

4. Conclusions

The substitution behaviour of *trans*-[PtClMe(SMe_2)$_2$] towards anionic and neutral ligands was investigated using stopped-flow spectrophotometry. The anionic ligands substitute the Cl^- ligand while the neural ligands substitute a SMe_2 ligand in the first process. All reactions follow the expected associative mode of activation as confirmed by large negative entropies of activation, a significant dependance of the reaction rate on the nucleophilicity of the entering ligands and a Linear Free Energy Relationship.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.015.

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