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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 $k_2 = 1.18 \pm 0.13$, $3.8 \pm 0.3$, $17.8 \pm 1.3$, $34.9 \pm 1.4$, $75.3 \pm 1.1\ mol^{-1}\ dm^3\ s^{-1}$ 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 $k_2 = 5.1 \pm 0.3$, $15.3 \pm 1.8$ 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 $\Delta H^{\neq} = 47.1 \pm 1.6$, $49.8 \pm 0.6$, $39 \pm 3$, $32 \pm 8$, $39 \pm 5$, $34 \pm 4$ and $31 \pm 3\ kJ\ mol^{-1}$ and $\Delta S^{\neq} = -107 \pm 5$, $-77 \pm 2$, $-104 \pm 9$, $-113 \pm 28$, $-85 \pm 18$, $-94 \pm 14$ and $-97 \pm 10\ J\ K^{-1}\ mol^{-1}$, respectively. Recalculation of $k_1$ to second-order units gives the following sequence of nucleophilicity: $MeOH < N_3^- < Br^- \sim py < 4 - Me - py \sim CN^- < I^- < SCN^- < Tu$ (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 $k_2 = 75.3 \pm 1.1$, $236 \pm 4$ 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 $\Delta H^{\neq} = 34 \pm 4$, $32 \pm 2$ and $39.3 \pm 1.7\ kJ\ mol^{-1}$ and $\Delta S^{\neq} = -94 \pm 14$, $-86 \pm 8$ 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]. $^1H$ 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%). $^1H$ 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]. $^1H$ 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. $^1H$ 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. $^1H$ 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]. $^1H$ 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-[$PtN_3Me(SMe_2)_2$] (**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. $^1H$ NMR analysis of a 10 mM solution in $CD_3OD$ prepared in a similar way verified the formation of the desired complex. $^1H$ 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

$^1H$ 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 $^1H$ 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 $^1H$ 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