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# Role of chelate substituents and *cis* σ-effect on the rate of ligand substitution at Pt(N–N–N) and Pt(N–N–C) centres †

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Four complexes of the type [Pt(N–N–X)Cl] (X = N or C) were tailor synthesized for mechanistic studies in methanol. The terdentate ligands included terpy, 4′-Ph-terpy, 4′-(2‴-$CF_3$-Ph)-terpy, and 4′-(2‴-$CF_3$-Ph)-6-Ph-2,2′-bipy. The rate of substitution of the chloro ligand by thiourea, *N*,*N*′-dimethylthiourea, and *N*,*N*,*N*′,*N*′-tetramethylthiourea was studied as a function of nucleophile concentration, temperature and pressure by using a stopped-flow technique. The observed pseudo-first-order rate constants for the substitution reactions obeyed the simple rate law $k_{obs} = k_2$[Nu]. Second-order kinetics and negative activation entropies and volumes support an associative substitution mechanism. At 298 K, the values of the second-order rate constant show a slight dependence on the nature of the moiety attached to the terpy ligand. Changing from a nitrogen σ-donor to a carbon σ-donor in the *cis* position, results in a deceleration of the substitution rate. The results suggest that the Pt–C bond in the *cis* position activates the metal centre in a different way than in the *trans* position.

## Introduction

Kinetic and mechanistic studies involving the Pt–C bond remain to be of considerable interest. This is because of the ability of the metal–carbon bond to labilize square-planar $d^8$ metal complexes through the kinetic *trans* effect.[1–8] Interesting results have been reported for substitution reactions of Pt(II) complexes containing metal–carbon bonds. All the studied complexes with a single Pt–C bond had this bond located *trans* to the leaving group. In general, these studies reported a very high substitution reactivity, with an increase in rate of up to six orders of magnitude.[9–15] This labilization is ascribed to the σ-bound carbon ligands such as alkyl and aryl groups, that have a large kinetic *trans* effect, plus back-bonding in case of the in-plane aryl ligand.[15–17] Mechanistically, the acceleration of the substitution process is linked to ground state destabilization due to the strong σ-electron donation along the C–Pt–X axis and stabilization of the transition state. Such tuning of the reactivity of Pt(II) complexes through electronic effects has made it possible to bring about a "Pd(II)-type" of reactivity in these Pt(II) complexes.[12,13,18–20] All in all, the reaction pathway remains associative in nature.

Turning to substitution reactions of Pt(II) complexes that have two carbon donors, these complexes mostly include two *cis* σ-bound carbon and two sulfur donor atoms in non-aqueous solvents. The most attractive property of these complexes is that displacement of the sulfur ligands occurs *via* a dissociatively activated pathway. This is promoted by bond weakening of the leaving group due to the *trans* influence of the strong Pt–C σ-donors and stabilization of the three-coordinate (14-electron) intermediate.[8,21–23] The factors that favour a dissociative pathway do not apply when carbon σ-donors that exhibit major π-acceptor properties, such as CO, are present. This is evident from the substitution behaviour of $[Pt(Ph)_2(CO)(Et_2S)]$, where the carbonyl group reduces the excess electron density on the metal centre and forces the reaction to follow an associative pathway.[24,25] Substitution reactions of complexes involving four metal–carbon bonds provided data for solvent exchange reactions of tetra-solvento square-planar complexes. The mode of action in these reactions remains associative in nature.[26–28] These results demonstrate that the extent of electron density on the metal centre plays a crucial role in dictating the nature of the substitution mechanism.

Whereas the influence of the *trans*-effect of a metal–carbon bond on the rate of square-planar substitution reactions is very significant, little is known about its *cis*-effect, and experimental results in the literature relating to this effect are contradictory.[29–35] This is due to the fact that the reactivity of Pt(II) complexes is affected differently when σ-donor, π-acceptor and steric properties of the *cis* ligand are varied. Despite these contradicting results, the general conclusion presented in most inorganic chemistry textbooks, is that the electronic effect of *cis* ligands is usually small when compared to that of the *trans* ligands in Pt(II) complexes.[36] Because of this, most of the studies involving the Pt–C bond have centred on labilization by ligands *trans* to the leaving group. A recent paper by Romeo and co-workers[37] reported a study on the effect of cyclometalation, where the metal–carbon bond was located in the *cis* position. From a comparison with literature data, they were able to conclude that the presence of a strong σ-donor carbon group decelerated the rate of ligand substitution due to the accumulation of electron density at the metal centre, making it less electrophilic.

Apart from the introduction of Pt–C bonds, it has also been shown that substituents on the terpy ligand also affect the substitution rates of the corresponding Pt(II) complexes.[38] It is therefore our aim in the present paper to shed more light on the role of the *cis* Pt–C bond and the influence that a substituted phenyl group, attached to the ancillary ligand (*trans* to the leaving group), may have on the metal centre and the leaving group. To achieve this, terdentate Pt(II) complexes of the type [Pt(N–N–N)] or [Pt(N–N–C)] with varying substituents on the central pyridine moiety were selected and their substitution behaviour was studied in detail.

## Experimental

### Materials and procedures

All reactions involving the synthesis of ligands were carried out in air, whereas coordination of the ligands to Pt(II) was performed under an inert atmosphere of nitrogen using standard

† Electronic supplementary information (ESI) available: A summary of the selected wavelengths used in the kinetic measurements, all measured rate constants and all the representative plots. See http://www.rsc.org/suppdata/dt/b3/b311595j/

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Schlenk techniques. Absolute ethanol (Merck) and 2-acetylpyridine (Aldrich) was used as supplied, whilst acetonitrile was purified by the method of Carlson *et al.*[39] Acetophenone (Riedel de Haen), benzaldehyde and *α*,*α*,*α*-trifluoromethyltolualdehyde(*o*) (Aldrich), were all purified by distillation prior to use. Ammonium acetate was dried in a vacuum dessicator over $P_2O_5$ for several days prior to use. Methanol was distilled over magnesium before use. The metal salts $K_2PtCl_4$ (Strem), $[Pt(PhCN)Cl_2]$ (Strem), lithium trifluoromethanesulfonate (Aldrich), lithium perchlorate (BDH Chemicals) and $AgSbF_6$ (Fluka AG) were used as supplied. The nucleophiles, thiourea (TU), 1,3-dimethyl-2-thiourea (DMTU), and 1,1,3,3-tetramethyl-2-thiourea (TMTU), were obtained from Aldrich and used as supplied. All other chemicals were of analytical reagent quality.

The ligand 2,2′:6′,2″-terpyridine was obtained from Aldrich, whereas 4′-phenyl-2,2′:6′,2″-terpyridine[40–42] and 4′-(2‴-$CF_3$-phenyl)-2,2′:6′,2″-terpyridine[43] were synthesized according to published methods. This included the ligand precursors [1-(2′-pyridyl)-3-(2″-$CF_3$-phenyl)-prop-2-ene-1-one][43,44] and *N*-{1-(2′-pyridyl)-1-oxo-2-ethyl}pyridinium iodide[45] required to synthesize 4′-(2‴-$CF_3$-phenyl)-2,2′:6′,2″-terpyridine.

**1-phenyl-3-(2″-$CF_3$-phenyl)-prop-2-en-1-one.** A suspension of *α*,*α*,*α*-trifluoromethyltolualdehyde (40 mmol) in absolute ethanol (100 ml) was cooled to 0 °C. Acetophenone (4.8 g, 40 mmol) was diluted in ethanol (10 ml) and then added to the cooled mixture. After stirring for 2 min at 0 °C, sodium hydroxide (40 ml, 1.0 M) was added drop-wise and the mixture was stirred for a further 3 h at 0 °C. Once stirring was complete, the product was precipitated from the solution by the addition of large quantities of ice water. The pale yellow product was filtered and thoroughly washed on the frit with 50% aqueous ethanol. The 1-phenyl-3-(2″-$CF_3$-phenyl)-prop-2-en-1-one was isolated as a pale yellow powder and dried *in vacuo*.

Yield 9.13 g (94%), m.p. 53–55 °C. GC/MS: *m*/*z* 243 ($M^+$). IR (KBr) *ν*(CO) 1664 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) *δ* 7.84(1H, AB, $^3J_{HH}$ 15.7 Hz, C*H*CO) 7.73(1H, AB, $^3J_{HH}$ 15.7 Hz, C*H*Ar).

**4-(2‴-$CF_3$-phenyl)-6-phenyl-2,2′-bipyridine.** The ligand precursors 1-phenyl-3-(2″-$CF_3$-phenyl)-prop-2-en-1-one (2.0 mmol) and *N*-{1-(2′-pyridyl)-1-oxo-2-ethyl}pyridinium iodide (0.72 g, 2.2 mmol) were added to a 100 ml round-bottomed flask. Ammonium acetate (10 g, excess) and absolute ethanol (8.0 ml) were added and the mixture heated to reflux for 60 min and thereafter allowed to cool. The ligand precipitated from the ambient reaction mixture upon cooling as a dirty white solid, which was filtered off and washed onto a glass frit with 50% aqueous ethanol. The impure ligand was recrystallised from ethanol (95%) to give a pale yellow powder.

Yield 0.52 g (70%), m.p. 129–130 °C. *Anal.* Calc. for $C_{26}H_{18}N_2$: C, 73.4; H, 4.0; N, 7.4%. Found: C, 73.4; H, 4.1; N, 7.4%. GC/MS.: *m*/*z* 376 ($M^+$). UV/Vis ($CH_3CN$): 305, 278sh, 259, 239 (π–π*). IR (KBr) ($cm^{-1}$): 626(w) 651(m) 688(m) 740(m) 774(m) 796(w) 1035(m) 1129(s) 1171(s) 1398(m) 1453(w) 1474(w) 1494(w) 1546(m) 1570(w) 1586(m) 1600(w). $^1H$ NMR ($CDCl_3$): 8.71(1H, d, $H^{6'}$) 8.68(1H, d, $H^{3'}$) 8.40(1H, s, $H^3$) 8.18(2H, m, $H^{2'',\ 6''}$) 7.84(1H, t, $H^{4'}$) 7.82(1H, m, $H^{6'''}$) 7.78(1H, s, $H^5$) 7.63(1H, d, $H^{3'''}$) 7.61(2H, m, $H^{4''',\ 5'''}$) 7.50(2H, m, $H^{3'',\ 5''}$) 7.46(1H, m, $H^{4''}$) 7.33(1H, m, $H^{5'}$).

### Synthesis of complexes

The complex [Pt(terpy)Cl]Cl.$2H_2O$ (Pt1) was prepared according to earlier literature methods.[46] $[Pt(4'\text{-phenyl-}2,2':6',2''\text{-terpyridine})Cl]^+$ (**Pt2**)[41,42] and $[Pt\{4'\text{-}(2'''\text{-}CF_3\text{-phenyl})\text{-}2,2':6',2''\text{-terpyridine}\}Cl]^+$ (**Pt3**)[43,44] were also synthesized following literature procedures. The method of Büchner *et al.*[47] was used to coordinate the ligands to Pt(II).

**[Pt{($CF_3$-Ph)Ph-bipy}Cl] (Pt4).** A mixture of $K_2PtCl_4$ (100 mg; 0.24 mmol) and 4-(2‴-$CF_3$-phenyl)-6-phenyl-2,2′-bipyridine {($CF_3$-Ph)Ph-bipy} (90 mg; 0.24 mmol) was refluxed in acetonitrile/water (10 ml; 1 : 1) for 48 h. The orange precipitate was filtered and washed onto a glass frit with large amounts of diethyl ether followed by smaller amounts of acetonitrile. The resulting solid was extracted *via* the sohxlet method with dichloromethane and excess solvent removed under reduced pressure. The precipitate was recrystallised by the slow diffusion of diethyl ether into a dimethylformamide solution containing the product. The solid product was recovered and dried *in vacuo*.

Yield 93 mg (64%). Molecular mass: 605.88 g $mol^{-1}$. *Anal.* Calc. for $C_{23}H_{14}ClF_3N_2Pt$: C, 45.59; H, 2.33; N, 4.62%. Found: C, 45.66; H, 2.03; N, 4.89%. UV/Vis ($CH_3CN$): 305, 278sh, 259, 239 (π–π*). IR (KBr) ($cm^{-1}$) 742 (m), 755 (m), 770 (m), 780 (m), 1036 (m), 1112 (s), 1128 (s), 1172 (s), 1313 (s), 1403 (m), 1417 (w), 1462 (w), 1478 (w), 1534 (m), 1584 (w), 1604 (m). $^1H$ NMR ‡ (DMSO-$d_6$) 8.93(1H, d, $H^{6'}$) 8.58(1H, d, $H^{3'}$) 8.33(1H, t, $H^{4'}$) 8.26(1H, s, $H^3$) 7.98(1H, s, $H^5$) 7.97(1H, d, $H^{3'''}$) 7.94(1H, t, $H^{5'}$) 7.88(1H, t, $H^{5'''}$) 7.78(1H, t, $H^{4''}$) 7.70(1H, d, $H^{6'''}$) 7.65(1H, d, $H^{3''}$) 7.52(1H, d, $H^{6''}$) 7.17(1H, t, $H^{5''}$) 7.06(1H, t, $H^{4''}$).

### Physical measurements and instrumentation

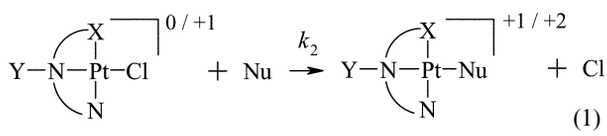
Elemental analyses were performed by the microanalytical laboratory at the University of Natal (Pietermaritzburg) and by Galbraith Laboratories Inc., Knoxville, TN, USA. Infrared spectra were recorded as KBr discs on either Shimadzu FTIR-4300 or Perkin Elmer Spectrum One spectrometers. $^1H$ NMR (200 MHz) were recorded on a Varian Gemini 200 spectrometer at 25 °C with chemical shifts referenced to $Si(CH_3)_4$. Mass spectra were obtained on a Hewlett Packard GC-MS using electron impact (EI) ionization. UV/Visible absorption spectra were recorded using either Varian Cary 100 Bio or Varian Cary 50 Probe spectrophotometers.

**Kinetics.** All kinetic measurements were performed under pseudo-first-order conditions using an Applied Photophysics SX.18MV (v4.33) stopped-flow system coupled to an online data acquisition system. High-pressure measurements were performed on a laboratory-made high-pressure stopped-flow instrument.[48] These instruments were thermostatted to within ±0.1 °C. The pseudo-first-order conditions were achieved by having the nucleophile in at least 10-fold excess. The ionic strength of the solution was maintained at 0.1 M using $LiClO_4$ or $LiCF_3SO_3$.

## Results

Substitution of coordinated chloride (reaction 1) from each of the four Pt(II) complexes (Chart 1) by three different nucleophiles (Nu), *i.e.* thiourea (TU), 1,3-dimethyl-2-thiourea (DMTU), and 1,1,3,3-tetramethyl-2-thiourea (TMTU), was investigated under pseudo-first-order conditions using conventional stopped-flow techniques. A typical kinetic trace recorded by mixing solutions of **Pt4** ($5.285 \times 10^{-5}$ M) and TU ($1.664 \times 10^{-3}$ M) in the stopped-flow instrument at an ionic strength of 0.1 M ($LiClO_4$), is shown in Fig. 1.

The pseudo-first-order rate constants, $k_{obs}$, calculated from the kinetic traces were plotted against the concentration of the



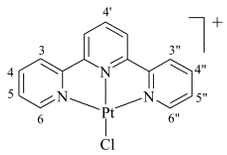

(1)

X = N (**Pt1, Pt2, Pt3**) or C (**Pt4**); Y= H, Ph, *o*-($CF_3$-Ph)

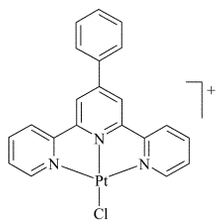
‡ The $^1H$ NMR spectrum is assumed to be that of the chloro complex since the substitution of $Cl^-$ by DMSO was found to be slow.

**Table 1** Summary of rate constants for the substitution of chloride by TU, DMTU and TMTU in methanol, $I$=0.1 M (**Pt1**, **Pt2** – $LiCF_3SO_3$; **Pt3**, **Pt4** – $LiClO_4$), $T$ = 298 K.

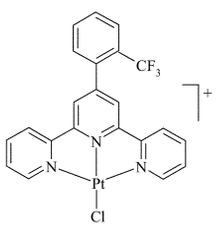
| | $k_2$, $M^{-1}s^{-1}$ | | | |
|---|---|---|---|---|
| Nucleophile | **Pt1** | **Pt2** | **Pt3** | **Pt4** |
| TU | 1494 ± 10 | 1258 ± 13 | 1933 ± 32 | 123.0 ± 0.3 |
| DMTU | 448 ± 10 | 377 ± 7 | 662 ± 3 | 72.0 ± 0.6 |
| TMTU | 82 ± 4 | 100 ± 3 | 144 ± 1 | 29.0 ± 0.5 |



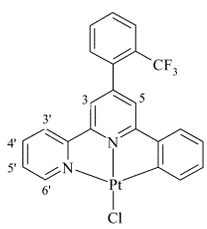
**[Pt1]** $[Pt(terpy)Cl]^+$



**[Pt2]** $[Pt\{4'\text{-Ph-terpy}\}Cl]^+$



**[Pt3]** $[Pt\{4'\text{-}(CF_3\text{-Ph})\text{-terpy}\}Cl]^+$



**[Pt4]** $[Pt\{4\text{-}(CF_3\text{-Ph})\text{-6-Ph-bipy}\}Cl]$

**Chart 1** Structural formulas of the investigated complexes.

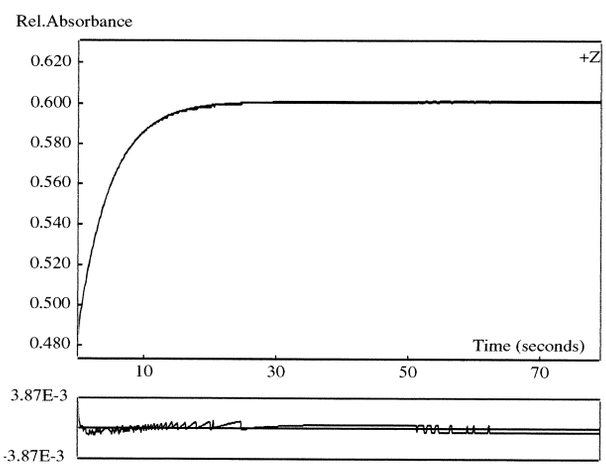



**Fig. 1** Fit of a single exponential and residuals (lower part) for the reaction of **Pt4** ($5.285 \times 10^{-5}$ M) with thiourea ($1.664 \times 10^{-3}$ M) followed at 348 nm, $I$=0.1 M ($LiClO_4$), $T$ = 298.15 K.

incoming nucleophiles. The values used represented an average of eight to twelve independent runs. Straight lines with zero intercepts were obtained for each of the nucleophiles, suggesting that the mechanism of the substitution can be represented by reaction (1)and the corresponding rate law given by eqn. (2)

$$k_{obs} = k_2[Nu] \quad (2)$$

Representative plots shown in Fig. 2 clearly indicate that the substitution reactions were first-order in the incoming nucleophile. The values of the second-order rate constants $k_2$, which results from the direct attack of the nucleophile as shown in reaction (1), were obtained from the slopes of these plots at 25 °C and are summarized in Table 1.

The temperature dependence of $k_2$, was studied over the range 15 to 35 °C. The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were calculated using the Eyring equation and are tabulated in Table 2.

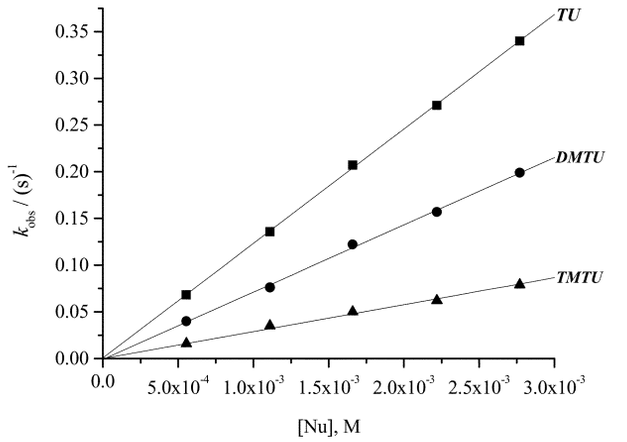



**Fig. 2** Dependence of the pseudo-first-order rate constants ($k_{obs}$) on the entering nucleophile concentration for chloride substitution on **Pt4** ($5.28 \times 10^{-5}$ M) in methanol, $I$=0.1 M ($LiClO_4$), $T$ = 298.15 K.

Pressure effects were studied for **Pt1**, **Pt2** and **Pt4** using TU and DMTU as the entering nucleophiles. Kinetic data in the pressure range 10–130 MPa was used to plot ln $k_{obs}$ against pressure. Since the concentration dependence plots were linear without any intercept, the pressure dependence of $k_{obs}$ is that of $k_2$. Good linear relationships, as shown in a representative plot in Fig. 3, were obtained, showing that the reactions are accelerated by pressure, which is typical for an associative substitution mechanism. This is in agreement with the negative activation entropy values obtained from the temperature dependence studies. The volumes of activation, $\Delta V^{\neq}$, calculated from the data in Fig. 3 are summarized along with the activation enthalpy and entropy values in Table 2.

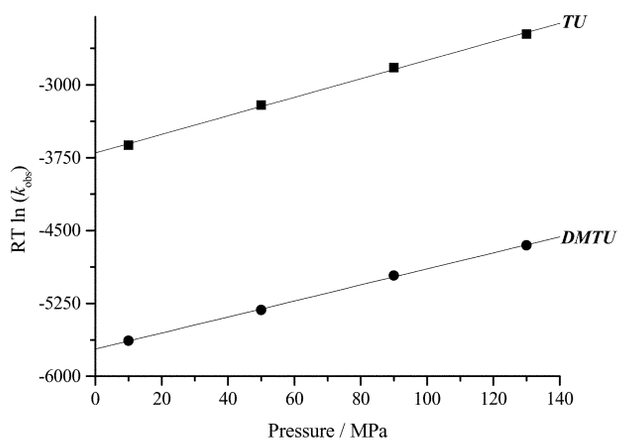



**Fig. 3** Determination of the activation volume, $\Delta V^{\neq}$, for the substitution of chloride in **Pt4** by TU and DMTU in methanol. [**Pt4**]=*ca.* 0.10 mM, [TU]=3.3 mM, [DMTU]=3.4 mM, $I$=0.1 M ($LiClO_4$), $T$ = 298 K.

## Discussion

Four complexes, $[Pt(terpy)Cl]Cl{\cdot}2H_2O$ (**Pt1**), $[Pt(4'\text{-Ph-terpy})Cl](SbF_6)$ (**Pt2**), $[Pt\{4'\text{-}(2'''\text{-}CF_3\text{-Ph})\text{-terpy}\}Cl](SbF_6)$ (**Pt3**) and $[Pt\{(4'\text{-}(2'''\text{-}CF_3\text{-Ph})\text{-6-Ph-2,2'-bipy}\}Cl]$ (**Pt4**) were synthesized by established procedures. The method of Kröhnke[45] was used to synthesize the ligands Ph-terpy, $(CF_3\text{-Ph})$-terpy and $(CF_3\text{-Ph})$Ph-bipy, details for the first two were published before.[41,43,44] Details of the synthesis and characterisation of the $(CF_3\text{-Ph})$Ph-bipy ligand are given in the Experimental section. These complexes were fully characterized analytically, chemically, and spectroscopically by IR, GC-MS and $^1$H NMR. The $^1$H NMR spectrum was recorded in deuterated DMSO to confirm the loss of proton signal brought about by deprotonation upon ortho-metallation to the Pt(II) metal. The spectral assignments for $[Pt\{(4'\text{-}(2'''\text{-}CF_3\text{-Ph})\text{-6-Ph-2,2'-bipy}\}Cl]$ (**Pt4**) were made with

**Table 2** Summary of activation parameters for the substitution of chloride by TU, DMTU and TMTU in methanol, $I$=0.1 M (**Pt1**, **Pt2** – $LiCF_3SO_3$; **Pt3**, **Pt4** – $LiClO_4$).

| Complex | Nucleophile | $\Delta H^{\neq}$/kJ mol$^{-1}$ | $\Delta S^{\neq}$/J K$^{-1}$ mol$^{-1}$ | $\Delta V^{\neq}$/cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|
| **Pt1** | TU | 28.7 ± 1.5 | −88 ± 5 | −6.2 ± 1.1 |
| | DMTU | 36.4 ± 1.1 | −73 ± 4 | −5.9 ± 0.2 |
| | TMTU | 35 ± 2 | −91 ± 8 | |
| **Pt2** | TU | 30.3 ± 0.2 | −84.4 ± 0.6 | −7.7 ± 0.8 |
| | DMTU | 38.3 ± 1.4 | −68 ± 4 | −5.7 ± 0.2 |
| | TMTU | 44.4 ± 1.5 | −58 ± 5 | |
| **Pt3** | TU | 30.0 ± 0.6 | −82 ± 2 | |
| | DMTU | 35 ± 2 | −74 ± 8 | |
| | TMTU | 31.5 ± 0.8 | −98 ± 3 | |
| **Pt4** | TU | 34.6 ± 0.5 | −89 ± 2 | −9.5 ± 0.3 |
| | DMTU | 38.1 ± 1.2 | −82 ± 4 | −8.2 ± 0.1 |
| | TMTU | 29 ± 5 | −119 ± 18 | |

**Table 3** Summary of selected bond lengths and angles relevant to the investigated complexes as obtained from the literature

| Complexes | **[Pt1]** [a]Pt-(terpy)Cl]$^+$ | **[Pt2]** [b][Pt{4′-Ph--terpy}Cl]$^+$ | **[Pt3]** [c][Pt{4′-($CF_3$-Ph)-terpy}Cl]$^+$ | **[Pt4]** [d][Pt{4-($CF_3$-Ph)-6-$C_6H_4$-bipy}Cl] |
|---|---|---|---|---|
| Bond lengths/Å | | | | |
| Pt–Cl | 2.307(2) | 2.313(2) | 2.286(3) | 2.305(2) |
| Pt–N1 | 2.018(5) | 2.039(9) | 2.004(10) | 2.038(6) |
| Pt–N3 | 2.030(5) | 2.013(10) | 2.014(10) | — |
| Pt–N2 | 1.930(4) | 1.936(9) | 1.931(8) | 1.948(5) |
| Pt–C (*trans* to N1) | — | — | — | 2.057(5) |
| Bond angles/° | | | | |
| N1–Pt–N3 | 161.8(2) | 161.7(4) | 162.3(3) | — |
| N1–Pt–C (*trans* to N1) | — | — | — | 161.4(2) |
| N2–Pt–Cl | 178.9(1) | 179.8(2) | 179.9(3) | 177.4(1) |
| N1–Pt–N2 | 81.1(2) | 81.0(4) | 81.1(4) | 81.3(2) |
| N2–Pt–N3 | 80.8(2) | 80.7(4) | 81.2(4) | — |
| N2–Pt–C (*trans* to N1) | — | — | — | 80.1(2) |

[a] [Pt(terpy)Cl]$^+$ $CF_3SO_3^-$; ref. 50. [b] [Pt{4′-Ph-terpy}Cl]$^+$ $BF_4^-$·$CH_3CN$; two cations per unit cell: data given are for the second cation only, as per ref. 41. [c] [Pt{4′-($CF_3$-Ph)-terpy}Cl]$^+$ $SbF_6^-$; ref. 43. [d] Ref. 44.

the aid of absolute value correlation spectroscopy (COSY) experiments and by comparison with the spectrum recorded for the very similar [Pt{6-(2-phenyl)-2,2′-bipyridine}Cl] reported by Constable and Cargill Thompson.[49] All analyses are in agreement with the structural formulas shown in Chart 1.

The synthesized complexes made it possible to quantify the effect of a σ-donor in the *cis* position relative to the leaving group by performing a comparative study on **Pt3** and **Pt4**. Complexes **Pt1** and **Pt2** were selected to establish the role (both electronic and steric) of the phenyl substituent in the 4′ position of the terpyridyl fragment in **Pt2**. This was extended by the introduction of a $CF_3$ group in the *ortho* position of the 4′-substituted phenyl ring of **Pt3**, and by the insertion of the carbon atom in the *cis* position of **Pt4**.

The substitution reactions of the investigated complexes can be interpreted in terms of the usual two-term rate-law in keeping with the associative mode of activation generally found for square planar complexes. This is supported by the activation parameters: the activation entropies are all large and negative, the activation enthalpies are relatively low, and the activation volumes are all negative. The moderate difference in the rate constants reflects the electronic role played by the nature of the ancillary ligands.

In comparing the reactivity of the complexes, it is clear from the data in Table 1 that the reactivity of **Pt1** is higher (factor of 1.2) than for **Pt2**, but lower (factor of 1.3) than for **Pt3**. The differences are only moderate and can be accounted for in terms of steric hindrance and σ-donicity of the phenyl substituent on the terpyridyl fragment. To separate these two factors, it is necessary to analyse the selected crystallographic data (bond lengths and angles) extracted from the literature and summarized in Table 3.

The molecular structures of these complexes show similarity in terms of planarity, bond lengths and angles. The coordination geometry of the Pt(II) centre in all the complexes is slightly distorted square planar with an angle of 161° deviating from linearity. The 4′-phenyl group lies out-of-plane with respect to the rest of the central pyridyl moiety of the ligand. There is a twist about the interannular bond such that the plane of the phenyl ring is at an angle of 33.3° with respect to the plane of the central ring for **Pt2**. In the cases of **Pt3** and **Pt4** the angles are 66.5 and 65.4°, respectively. This out-of-plane distortion rules out any possible π interaction between the 4′-phenyl ring and the terpyridyl or bipyridyl fragment and any extension of π back-bonding, *i.e.*, π electronic communication between the two is not possible. The proximity of the phenyl ring to the metal centre also eliminates any possible steric hindrance for the entering nucleophile. The effectiveness of this would have been larger if there was direct interaction between the phenyl ring and the metal atom as in the case of substitution reactions involving [Pt(bipy)(Ph)Cl][37] and *trans*-[$Pt(PEt_3)_2$(R)Cl].[51]

In the present case the moderate difference in the rate of substitution on all the complexes is purely an electronic effect. The phenyl system in **Pt2** is a better σ-donor than that of **Pt3** due the presence of the $CF_3$-moiety, which withdraws electrons from the ring. Therefore, the electron donating phenyl ring reduces the π-acceptor abilities of the terpy ligand in the case of **Pt2**, whereas the electron withdrawing $CF_3$ substituted phenyl ring increases them in the case of **Pt3**. The net effect is that π back-bonding of the metal orbitals with the terpy ligand is

slightly weaker in **Pt2** than in **Pt1**, whereas it is more effective in **Pt3**. Here the interactions between $d_{xz}$ and $d_{yz}$ and the empty/anti-bonding π orbitals play a minor role; the main interaction responsible for the enhanced reactivity is between the empty $p_z$ orbital, which is filled with electrons in the transition state, and the π-acceptor orbitals on the ligand.[30] This means that stabilization of the transition state through π back-bonding and creation of a more electrophilic metal centre, promotes nucleophilic approach to the reaction centre and enhances the formation of a new bond in **Pt3**. The retardation effect observed between **Pt1** and **Pt2** has previously been noted when a methoxy (electron donating) group was attached to the ancillary ligand.[5]

To pin down the role of the *cis* σ-effect, the reactivities of **Pt3** and **Pt4** need to be compared. The data in Table 2 suggest that the introduction of the Pt–C bond in the *cis* position to the chloride atom reduces its lability by a factor of 16 when the entering nucleophile is TU, with similar retardation on the rates of substitution being observed for the other entering nucleophiles. This decrease in reactivity is due to the accumulation of electron density at the metal centre, making it less electrophilic than the analogous **Pt3** complex. In doing so, the rate of substitution decreases, since the incoming nucleophile is repelled by the increase in electron density around the metal centre. The *cis* effect of the carbon atom reported in this study has been shown to decrease the lability of complexes whose reactivity is enhanced by the presence of strong π-electron withdrawing backbone.[37,52]

It is worth noting that these findings indicate that the *cis* and *trans* carbon σ-donors influence the lability of the leaving group in a different way. When positioned *trans* to the X group (C–Pt–X), the well-known *trans* effect[53] takes control of the reaction as a result of the ground state labilization (*trans* influence) and transition state stabilization (*trans* effect).[5,13,19] This usually involves the elongation of the Pt–X bond[13,54,55] and corresponding shortening of the aryl-metal bond,[56] which if present in the same plane, promotes π back-bonding. The net effect of these two factors is an acceleration of the rate of substitution. The retardation observed when Pt–C is in the *cis* position is due to the accumulation of electron density around the metal centre as already mentioned. The fact that this seems to have a less significant effect on the Pt–X bond length is probably due to lack of direct overlap of the orbitals of the two atoms *cis* to each other, unlike in the case when they are *trans* to each other. This means that while the Pt–C *trans* effect increases the ground state destabilization of Pt(II) complexes, the Pt–C *cis* effect has little if any of this character.[52]

The activation parameters in Table 3 are typical for associatively activated processes, since all the activation entropies are largely negative, suggesting a highly ordered transition state. This order arises from the back donation of electron density from the metal centre to the terpy or bipyridine ligand. In addition, the enthalpy values are all very low, indicating the ease of bond formation as a result of the electrophilic nature of the metal centre. Furthermore, the suggested mechanism is supported by the negative volumes of activation.[57] The values are typical for associative substitution reactions in square-planar complexes of Pd(II) and Pt(II).[58,59] The difference in reactivity between **Pt4** and the other complexes cannot be linked to the activation enthalpy or entropy, since the experimental error is larger than the observed differences in most cases.

In terms of steric effects, substitution of chloride shows a clear dependence on the steric hindrance of the entering nucleophiles. The sterically less hindered nucleophile thiourea (TU) has the highest substitution rate, whereas the most sterically hindered nucleophile, *N*,*N*,*N*′,*N*′-tetramethylthiourea (TMTU), reacts significantly slower. This trend is accompanied by an increase in activation enthalpy, and almost constant activation entropy and activation volume values (see Table 2). If the relative rates for the reactions with TU, DMTU and TMTU are compared for the four complexes (for TU : DMTU : TMTU: **Pt1** 18 : 5.5 : 1; **Pt2** 13 : 3.8 : 1; **Pt3** 13 : 4.6 : 1; **Pt4** 4.2 : 2.5 : 1), it can clearly be seen that the reactions with the **Pt4** complex are less sensitive to steric hindrance of the incoming ligand. This can easily be explained by the relatively large Pt–C distance (2.057(5) Å for **Pt4**) that is due to the large *trans* influence of the carbon atom in comparison with the smaller Pt–N3 distance (2.030(5), 2.013(10), and 2.014(10) Å, for **Pt1**, **Pt2** and **Pt3**, respectively) in the other complexes. This reduces the steric interactions of the entering nucleophile with the *cis* groups of the terpy moiety, resulting in a complex that has a reduced steric discrimination in comparison with **Pt1**, **Pt2** and **Pt3**.

## Conclusions

The lability of coordinated chloride in the studied complexes is controlled by the electrophilicity of the metal centre. This in turn depends on the properties of the terpyridyl fragment. It is clear that the introduction of substituents on the ancillary terpyridyl ligand dictates the extent of π-electron withdrawal through back-bonding effects. The presence of electron donating substituents (phenyl ring in **Pt2**) on the terpy fragment decreases the rate of substitution, whereas the addition of an electron withdrawing (*o*-$CF_3$-phenyl in **Pt3**) entity has the opposite effect. The most significant feature of this work is the elucidation of the role the *cis* Pt–C bond has on the lability of the leaving group. The *cis* and *trans* σ-effects have an opposite net effect. While the latter enhances the rate of substitution through ground-state destabilization, the former decelerates the process through the accumulation of electron density at the metal centre. This does not only prevent the approach of the nucleophile, but also suppresses the stabilization of the transition state. The mode of activation remains associative in nature throughout the studied systems.

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