Controlling the extent of π -backbonding in platinum(II) terpyridyl systems: a detailed kinetic, mechanistic and computational approach[†]

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The rate of substitution of the chloride ligand from [Pt(terpy)Cl]⁺ (Pt1) (where terpy = 2,2':6',2''-terpyridine) and its corresponding analogue [Pt('Bu₃terpy)Cl]⁺ (Pt2) (where 'Bu₃terpy = 4,4',4"-tri-*tert*-butyl-2,2':6',2"-terpyridine) by a series of neutral and anionic nucleophiles, viz. thiourea (TU), 1,3-dimethyl-2-thiourea (DMTU), 1,1,3,3-tetramethyl-2-thiourea (TMTU), iodide (I⁻) and thiocyanate (SCN⁻), was determined under pseudo first-order conditions as a function of concentration and temperature using standard stopped-flow spectrophotometric techniques. The observed pseudo first-order rate constants for the substitution reactions obeyed the simple rate law $k_{obs} = k_2$ [nucleophile]. Second-order kinetics and negative activation entropies support an associative mode of activation. The rate of substitution of chloride is observed to decrease with an increase in the steric bulk of the neutral nucleophiles, whilst rate of substitution by I⁻ was observed to be faster than that by SCN⁻, in correlation with their polarizability and the softness of the metal centre. A comparison of the second-order rate constants, k_2 , at 298 K, obtained for the substitution reactions of Pt1 and Pt2 shows that the introduction of strong σ -donating groups on the periphery of the terpyridyl backbone in Pt2 results in a corresponding decrease in the reactivity. DFT calculations at the B3LYP/LACVP** level of theory for the two complexes, Pt1 and Pt2, and a series of similar analogues containing either electron-donating or electron-withdrawing groups in the periphery positions demonstrate that the introduction of electron-donating groups decreases the positive charge on the metal centre and increases energy separation of the frontier molecular orbitals ($E_{\text{HOMO}} - E_{\text{LUMO}}$) of the ground state platinum(II) complexes leading to a less reactive metal centre whilst the introduction of electronwithdrawing groups has an opposite effect leading to increased reactivity of the metal centre.

Introduction

Mechanistic investigations into ligand substitutions at squareplanar centres of d^8 transition metal ions such as platinum(II) and palladium(II), have been extensively reviewed and remain among the most investigated and understood dynamic processes in chemistry.¹⁻⁷ The bulk of information relating to four-coordinate planar substitution mechanisms comes from the reactions of Pt(II) substrates, where a combination of redox stability and relatively low reactivity allow for the synthesis of specifically designed substrates and subsequent kinetic studies of these.²⁻⁵ In addition, substitution reactions of square-planar Pt(II) complexes continue to attract attention due to their applications in homogenous catalysis⁸ and anti-tumour treatment.^{9,10}

The substantial amount of kinetic and thermodynamic data collected in the last few decades clearly demonstrate that the reaction mechanisms of square-planar complexes is associative in nearly all cases,²⁻⁵ with only a limited number of complexes exhibiting a mechanistic changeover under specific conditions.¹¹⁻¹⁴

In recent years, mechanistic investigations into the substitution processes at square-planar Pt(II) centres have focused on tuning the reactivity of the metal centre.¹⁵⁻¹⁸ These studies have all demonstrated the influence of the ligand structure about the metal centre on the substitution behaviour of platinum complexes.

Van Eldik et al.^{17,18} systematically studied the effect of progressively adding π -acceptor ligands (*viz.* pyridine ligands) to the chelating ligands in a series of platinum(II)-aqua complexes of the type $[Pt(L)(OH_2)]^{2+}$ (where L = a tridentate N-donor chelate or NH₃/bipyridine). The authors found that the reactivity of the associative substitution reaction on Pt(II) can be increased in a stepwise manner by the addition of the π -acceptor ligands, with reactivity ratio of the complexes with increasing π -acceptor ligands, viz. $[Pt(aaa)(OH_2)]^{2+}$: $[Pt(apa)(OH_2)]^{2+}$: $[Pt(ppp)(OH_2)]^{2+}$ (where aaa = diethylenetriamine; apa = 2,6-bis-aminomethylpyridine and ppp = 2,2':6',2''-terpyridine) being approximately 1:3.5:5600, in the case of substitution of the aqua moiety by thiourea. The experimental data also suggested that the π -cis effect was greater than the π -trans effect. The authors concluded that the reactivity of these Pt(II) complexes resulted from the electrophilicity of the metal centre, as a direct result of electron back-donation of incoming electron density to the ligand orbitals, which is further enhanced by electronic communication between π -acceptor ligands.

Density functional theory (DFT) calculations showed that the addition of π -acceptor ligands resulted in an increase in the positive charge on the metal and a corresponding decrease in

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the energy separation of the frontier molecular orbitals ($E_{LUMO} - E_{HOMO}$) of the ground state Pt(II) complexes.¹⁷

Lowe *et al.*¹⁹ demonstrated that the presence of a substituent at the 4'-position of the terpyridyl system alters the electronic properties of the terpyridyl ligand. By studying the rates of hydrolysis of five (4'-substituted-2,2':6',2''-terpyridine)platinum(II) (*n*-propylamine) complexes and subsequent analysis using the Hammett equation, the authors found that in the case of electrondonating groups they obtain a positive ρ -value. This led them to conclude that the presence of the substituent at the 4'-position leads to a build-up of electron density in the transition state thus rendering the metal centre less electrophilic. The authors also suggested that this effect can be reduced by the introduction of electron-withdrawing groups.

Indeed, work in our laboratories has also demonstrated that the introduction of different *ortho*-substituted phenyl groups at the 4'-position of the terpyridyl backbone can moderately influence the reactivity of the platinum(II) centre.¹⁵ In the case of substitution of chloride by the neutral nucleophiles thiourea, 1,3-dimethyl-2-thiourea and 1,1,3,3-tetramethyl-2-thiourea, we find that the reactivity of [Pt{4'-(phenyl)terpy}Cl]⁺ is slightly less than that of the parent [Pt(terpy)Cl]⁺ due to their presence of the weak, electron-donating phenyl group. However, the reactivity of [Pt{4'-(phenyl)terpy}Cl]⁺ is slightly greater than both [Pt{4'-(phenyl)terpy}Cl]⁺ and [Pt(terpy)Cl]⁺ due to the presence and electron-withdrawing nature of the *ortho*-CF₃-phenyl substituent in the 4'-position.

In keeping with this trend, this work describes, by means of a kinetic and computational investigation, the possibility of controlling the extent of π -backbonding by the simple introduction of either electron-donating or electron-withdrawing groups at the 4, 4' and 4" positions of the terpyridyl backbone.

Experimental

Materials & methodology

Reactions used in the synthesis of the platinum(II) terpyridyl complexes were all carried out in air unless otherwise stated. Potassium tetrachloroplatinate (K₂PtCl₄, 99.99%), 2,2':6',2"-terpyridine (terpy, 98%), 4,4',4"-tri-*tert*-butyl-2,2':6',2"-terpyridine ('Bu₃terpy, 97%), sodium perchlorate monohydrate‡ (NaClO₄· H₂O, 98%), lithium trifluoromethanesulfonate (LiCF₃SO₃, 96%), 1,5-cyclooctadiene (COD, 99%) and acetonitrile (CH₃CN, \geq 99.9%) were obtained from Aldrich and were used without further purification. Silver perchlorate‡ (AgClO₄, 99.998%, Aldrich) was stored under nitrogen and used as supplied. Perchloric acid (HClO₄, 70% solution) and hydrochloric acid (HCl, 32% solution) was obtained from Saarchem and used as supplied. Methanol (Saarchem) was distilled over magnesium before use.²⁰

The nucleophiles, thiourea (TU, 99%), 1,3-dimethyl-2-thiourea (DMTU, 99%), 1,1,3,3-tetramethyl-2-thiourea (TMTU, 98%)§ and sodium thiocyanate (NaSCN, 98%) were obtained from Aldrich and used without further purification. The nucleophile,

sodium iodide (NaI, 99%) was obtained from Saarchem and used as supplied. Ultrapure water (Modulab Systems) was used for all aqueous reactions. All other chemicals were of analytical reagent quality.

The platinum(II) precursor, dichloro(1,5-cyclooctadiene)platinum(II) (1)²¹ and the corresponding platinum(II) terpyridyl complexes, [Pt(terpy)Cl]Cl·2H₂O (Pt1)²² and its corresponding analogue [Pt('Bu₃terpy)Cl]ClO₄ (Pt2),²³ were synthesized *via* known literature procedures.

Synthesis of the platinum(II) terpyridyl complexes

Dichloro(1,5-cyclooctadiene)platinum(II) (1). To a filtered, aqueous solution of potassium tetrachloroplatinate (K₂PtCl₄) (2.18 mg, 5.23 mmol) in water (55 ml), was added glacial acetic acid (35 ml) and 1,5-cyclooctadiene (COD) (2.1 ml, 17 mmol). The resultant mixture was heated, with vigorous stirring, at 90 °C for approximately 30 min. During this period a colour change from the initial deep-red solution to a pale-yellow solution was observed. The product, dichloro(1,5-cyclooctadiene)platinum(II) (1), precipitated as fine pale-yellow crystals before the 30 min had elapsed. After 30 min, further precipitation of the product was induced by concentrating the solution under reduced pressure to a final volume of approximately 10 ml. The pale-yellow, crystalline product was collected by filtration and washed with successive 50 ml portions of water, ethanol and diethyl ether and thereafter oven-dried at 100 °C for 1 h to afford the title complex, dichloro(1,5-cyclooctadiene)platinum(II) (1) of sufficiently high purity.

Yield: 1.75 g (88%). Anal. calc. for $PtC_8H_{12}Cl_2$: C, 25.7; H, 3.2; N, 0.0. Found: C, 26.2; H, 3.5; N, 0.0.

[Pt(terpy)Cl]Cl-2H₂O (Pt1). To a stirred suspension of $[Pt(COD)Cl_2]$ (1) (500 mg, 1.34 mmol) in water (30 ml), was added 2,2':6',2"-terpyridine (313 mg, 1.34 mmol). The resultant mixture was warmed to *ca.* 45–50 °C with stirring. After approximately 15 min, the suspended metal complex completely dissolved to afford a clear, orange–red solution which was cooled to room temperature and filtered to remove any unreacted [Pt(COD)Cl₂]. The filtrate was then evaporated under reduced pressure to afford an orange–red solid, [Pt(terpy)Cl]Cl-2H₂O (Pt1), which was collected by filtration, washed thoroughly with diethyl ether and air-dried.

Yield: 0.65 g (90%). Anal. calc. for $PtCl_2O_2C_{15}H_{15}N_3$: C, 33.7; H, 2.8; N, 7.9. Found: C, 33.5; H, 2.7; N, 7.7. IR (KBr) cm⁻¹: 465(m), 519(m), 722(m), 781(vs), 1029(m), 1091(w), 1245(sh), 1247(mb), 1284(m), 1316(ms), 1400(s), 1453(s), 1481(s), 1605(s), 3047(mb), 3409(sb).

[Pt('Bu₃terpy)Cl]ClO₄ (Pt2). K₂PtCl₄ (415 mg, 1.00 mmol) was dissolved in a solution of 50% aqueous acetonitrile (30 ml) and the resulting solution filtered to remove any metallic platinum. To the stirred platinate solution was added 4,4',4"-tri-*tert*-butyl-2,2':6',2"-terpyridine (402 mg, 1.00 mmol). The resulting mixture was heated to reflux for 24 h. The resulting yellow solution was filtered into 100 ml of a 0.50 M aqueous solution of NaClO₄. The filtrate was slowly cooled and the resulting yellow precipitate was collected by filtration and washed with dilute hydrochloric acid (0.1 M). The bright-yellow solid was recrystallized by vapour diffusion of diethyl ether into an acetonitrile solution of the

[‡] Perchlorate salts are potentially explosive and should be handled with caution and in small amounts.

[§] Thiourea and its substituted derivatives are suspected carcinogens and the necessary safety precautions must be adhered to when handling these reagents.

crude product to afford yellow needle-like crystals of the required platinum(II) complex.

Yield: 0.53 g (71%). Anal. calc. for PtCl₂O₄C₂₇H₃₅N₃: C, 44.3; H, 4.8; N, 5.7. Found: C, 44.4; H, 4.8; N, 5.7. IR (KBr) cm⁻¹: 464(m), 487(w), 552(sh), 609(s), 623(s), 739(m), 825(sh), 870(s), 889(s), 907(m), 918(m), 1027(m), 1091(vs), 1179(m), 1258(s), 1297(w), 1374(m), 1405(sh), 1416(s), 1430(s), 1467(s), 1480(s), 1560(m), 1615(vs), 2014(s), 2872(m), 2909(m), 2959(vs), 3096(s), 3203(s), 3424(wb). ¹H NMR (CD₃CN): 1.44 (s, 18H, ¹Bu), 1.53 (s, 9H, ¹Bu), 7.73 (dd, 2H, ³J_{HH} = 6.05 Hz, ⁴J_{HH} = 2.10 Hz, H₅) 8.65 (d {broad ¹⁹⁵Pt satellites}, 2H, ³J_{HH} = 6.05 Hz, H₆). ¹³C NMR (CD₃CN): 30.28; 30.54 (*CMe*₃), 37.11; 38.08 (*CMe*₃), 122.6, 124.3, 126.4, 151.6, 155.4, 159.3, 168.4, 168.5. ¹⁹⁵Pt NMR (CD₃CN) = -734.

Computational modelling

Preliminary modelling of the complexes was performed using the computational software package Spartan 04 for Windows,^{24,25} using the B3LYP²⁶ density functional method (DFT)^{27,28} and the LACVP+** (Los Alamos core valence potentials)²⁹ pseudopotential basis set. B3LYP relates to the hybrid functional Becke's threeparameter formulation,²⁶ which has been proven to be superior to traditional functionals. The LACVP basis set employs effective core potentials for K-Cu, Pb-Ag, Cs-La and Hf-Au while Pople's 6–31G** basis set describes second and third row s- and p-block elements.^{30,31} The performance of the DFT calculations at the chosen level of theory was gauged by comparison of the calculated structures to X-ray structure of [Pt('Bu₃terpy)Cl]⁺ and of similar terpy analogues of platinum(II), *viz.* [Pt(terpy)(OMe)]^{+, 23,32}

Preparation of complex and nucleophile solutions for kinetic analysis

The 'solvent' used in the preparation of complex and neutral nucleophile solutions was prepared by dissolving the required quantity of either $\text{LiCF}_3\text{SO}_3\P$ or NaClO_4 in freshly distilled methanol to afford a solution of concentration 0.10 M. Since neither the triflate ion, CF_3SO_3^- , nor the perchlorate ion, CIO_4^- , is known to coordinate to Pt(II),³³ the substitution reactions of the platinum complexes (**Pt1**–LiCF₃SO₃, **Pt2**–NaClO₄) were performed in these media.

Solutions of the metal complex were prepared by dissolving the required amount of the metal salt in 50 ml of the constant ionic strength solution prepared above.

Solutions of the neutral nucleophiles, *viz*. TU, DMTU and TMTU, were prepared by dissolving a known amount of the required nucleophile in 100 ml of a solution having fixed ionic strength (*i.e.* the 0.1 M methanolic solution of either LiCF₃SO₃ or NaClO₄) to afford a final concentration that was *ca.* 50 times greater than that of the metal complex, whilst maintaining an ionic strength of 0.1 M. Subsequent dilutions with the same solution of fixed ionic strength afforded a series of concentrations, in the

order of 10, 20, 30, 40 and 50 times the concentration of the metal complex.

Solutions of the anionic nucleophiles, I^- and SCN⁻, were prepared by dissolving known amounts of the appropriate sodium salts and either LiCF₃SO₃ or NaClO₄·H₂O in 100 ml of distilled methanol to afford a solution of final concentration that was *ca*. 50 times greater than that of the metal complex and an ionic strength equal to 0.1 M. Subsequent dilutions with the solution of fixed ionic strength (*i.e.* the 0.1 M methanolic solution of either LiCF₃SO₃ or NaClO₄) afforded a series of concentrations, in the order of 10, 20, 30, 40 and 50 times the concentration of the metal complex.

Instrumentation & physical measurements

Elemental analyses were performed at the Institute for Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstr. 1, Erlangen, Germany. NMR spectra (¹H, ¹³C and ¹⁹⁵Pt) were recorded on a Varian Gemini 500 spectrometer at 25 °C, with chemical shifts referenced to Si(CH₃)₄. Infrared spectra were recorded using KBr discs on a Perkin Elmer Spectrum One FTIR spectrometer. UV/Visible absorption spectra were recorded using a Varian Cary 100 Bio spectrophotometer.

All kinetic measurements were performed under pseudo firstorder conditions using, initially, UV/Visible absorption spectra to determine the suitable wavelength at which kinetic investigations could be performed. All substitutions were observed to reach completion in less than sixteen minutes and subsequently an Applied Photophysics SX.18MV (v4.33) stopped-flow system coupled to an online data acquisition system was used to monitor the kinetic process. All measurements were performed in a thermostatted environment to within ± 0.1 °C. All data were graphically analysed using the software package, Origin 5.0[®].³⁴

All ligand substitutions were followed for at least eight half-lives.

All kinetic measurements were best described by a single exponential equation. The observed pseudo first-order rate constants, k_{obs} , were calculated using the online non-linear least-squares fit of exponential data to eqn (1):³

$$A_t = A_o + (A_o - A_{\infty})\exp(-k_{obs}t) \tag{1}$$

where A_0 , A_1 and A_{∞} represent the absorbance of the reaction mixture initially, at time *t* and at the end of the reaction respectively.

The dependence of the rate constant on the incoming nucleophile concentration was analysed in this manner for all nucleophiles whilst maintaining the temperature at 25 °C. The second-order rate constant, k_2 , for the reaction of each metal complex with a particular nucleophile was obtained from the slope of a linear regression of a plot of the observed rate constants, k_{obs} , *versus* the nucleophile concentration using Origin 5.0^(B).³⁴ All plots can be described by eqn (2):³

$$k_{\rm obs} = k_2 [\rm Nu] \tag{2}$$

The dependence of the rate constant on temperature was conducted in a similar manner, with the nucleophile concentration being held constant at 30 times the concentration of the metal complex whilst varying the temperature from 15 to 35 °C in 5 °C intervals. The activation parameters, ΔH^* and ΔS^* , were determined by applying the values of the observed rate constants, k_{obs} , to the Eyring equation.³

[¶] The choice of the lithium salt was found to be dependent upon the interaction of the metal complex when reacted with solutions of the nucleophile (when prepared using the sodium perchlorate "solvent" medium). When the complex **Pt1** was reacted with nucleophile solutions containing sodium perchlorate, precipitation of the metal complex was observed. It was for this reason that lithium triflate was chosen for the reactions with **Pt1**.

Results

Substitution of coordinated chloride from each of the Pt(II) complexes (Scheme 1) by both neutral, *viz*. thiourea (TU), 1,3-dimethyl-2-thiourea (DMTU), and 1,1,3,3-tetramethyl-2-thiourea (TMTU), and ionic nucleophiles, *viz*. iodide (I⁻) and thiocyanate (SCN⁻), was investigated under pseudo-first-order conditions using conventional stopped-flow techniques.



Scheme 1

All kinetic traces were described by perfect single exponentials (Fig. S1, ESI).† The pseudo first-order rate constants, k_{obs} , calculated from the kinetic traces were plotted against the concentration of the 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 any reverse reaction or influence or the solvent was negligible and that the mechanism of the substitution can be represented by Scheme 1 and the corresponding rate law given by Equation 2.

Representative plots shown in Fig. 1 clearly indicate that the substitution reactions were first-order with respect to 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 Scheme 1 were obtained from the slopes of these plots at 25 °C and are summarized in Table 1.



Fig. 1 Dependence of the pseudo first-order rate constants (k_{obs}) on the entering nucleophile concentration for chloride substitution on Pt2 (0.170 mM) in methanol, I = 0.1 M (NaClO₄), T = 298.15 K.

The activation parameters, ΔH^* and ΔS^* , were calculated using the Eyring equation³ and are tabulated in Table 1. A typical plot is shown in Fig. 2.

Discussion

In the current study, two platinum(II) complexes, *viz*. [Pt(terpy)Cl]⁺ (Pt1) and its corresponding analogue [Pt(^tBu₃terpy)Cl]⁺ (Pt2), were synthesized and their substitution behaviour studied in order to investigate the possibility of controlling the extent of π -backbonding in platinum(II) terpyridyl systems.

The presence of the *tert*-butyl groups at the 4, 4' and 4" positions of the terpyridyl fragment in **Pt2** made it possible to investigate the role of strong electron-donating groups in controlling the extent of π -backdonation from the metal centre.

The substitution reactions of the investigated complexes can be interpreted in terms of the usual rate law in keeping with the associative mode of activation generally found for square-planar

Table 1 Summary of rate constants and activation parameters and the corresponding standard deviations^{*a*} for the substitution of chloride by neutral (TU, DMTU and TMTU) and ionic (I⁻ and SCN⁻) nucleophiles in methanol, I = 0.1 M (NaClO₄)

Complex	Nucleophile	$k_2 / \mathbf{M}^{-1} \mathbf{s}^{-1}$	$\Delta H^{\neq}/\mathrm{kJ}~\mathrm{mol}^{-1}$	$\Delta S^{\neq}/J \mathrm{K}^{-1} \mathrm{mol}^{-1}$	
	TU	1494 ± 10	28.7 ± 1.5	-88 ± 5	
	DMTU	448 ± 10	36.4 ± 1.1	-73 ± 4	
	TMTU	82 ± 4	35.0 ± 2.0	-91 ± 8	
	I-	243 ± 4	47.4 ± 3.2	-42 ± 11	
	SCN⁻	17 ± 0.2	48.0 ± 2.0	-61 ± 1	
Pt1					
I	TU	452 ± 5	33.6 ± 0.2	-82 ± 1	
++	DMTU	152 ± 1	39.9 ± 1.0	-70 ± 4	
	TMTU	38 ± 0.2	35.5 ± 0.2	-96 ± 1	
	I-	60 ± 0.4	49.0 ± 0.2	-47 ± 1	
	SCN-	3 ± 0.02	57.2 ± 0.2	-43 ± 1	

Pt2

^{*a*} Standard deviations obtained for k_2 are those of the slope of the plot of k_{obs} versus nucleophile concentration. Standard deviations for activation parameters obtained are those from the slope (ΔH^*) and y-intercept (ΔS^*) obtained from a plot of $\ln(k_2/T)$ versus 1/T.



Fig. 2 Plots of $\ln(k_2/T)$ versus 1/T for the reaction of **Pt2** with a series of neutral and ionic nucleophiles at various temperatures in the temperature range 15 to 35 °C.

complexes. This is well supported by the determined activation parameters: the activation entropies are all large and negative whilst the activation enthalpies are relatively low. The marked difference in the rate constants of the two complexes reflects the role played by the introduction of strong electron-donating groups at the ancillary positions of the terpyridyl backbone.

From Table 1, it can be seen that the reactivity of **Pt1** is greater than that of **Pt2** in all cases. In the case of the neutral nucleophiles; TU, DMTU and TMTU, the increase in steric hindrance of the nucleophiles is reflected by the corresponding decrease in the rate constant, since the bulkier nucleophiles find it increasingly difficult to closely approach the metal centre. This trend is accompanied by relatively constant values of activation enthalpy, ΔH^* . The mechanism remains associative in all cases.

In the case of the anionic nucleophiles, the rate of substitution of the chloride species in **Pt1** and **Pt2** was lower than that observed for substitution by the neutral nucleophiles, *ca.* 6 times slower when comparing substitution of chloride from **Pt1** by TU and I⁻ respectively. This reactivity trend is expected, based on the nucleophilicities $(n_{P_1}^\circ)$ found for monocationic complexes of platinum(II),^{3,35-37} varying in the order amine $< Cl^- < NO_2^- < N_3^- < Br^- < SCN^- < I^- < TU < SeCN^-$ and correlates well with previous studies.^{17,38} Again, the determined activation parameters support an associative mode of substitution.

Thus, the experimental data obtained in the current study supports the conclusions drawn by both Lowe *et al.*¹⁹ and Jaganyi *et al.*,¹⁵ in that again we notice that electron-donating groups attached in the ancillary positions of the terpyridyl backbone do in fact result in a deceleration in the rate of ligand substitution. Also, unlike the above-mentioned studies, the substituents in the ancillary positions are not limited to the *trans* position, where a combination of the well-known *trans*-effect²⁻⁵ and the electron-donating properties of the substituent might work *anti* to each other.

The question therefore remains as to how the presence of *tert*-butyl groups, *i.e.* the electron-donating groups, controls the extent of π -backbonding in these terpyridyl systems. In a study by Cummings *et al.*³⁹ on the photophysical properties on platinum(II) complexes of 4'-chloro-2,2':6',2''-terpyridine (Cl-

terpy) and 4,4',4''-trichloro-2,2':6',2''-terpyridine (Cl₃-terpy), *i.e.* terpyridyl ligands containing electron-withdrawing substituents in the ancillary positions. Their studies indicated that the metal-to-ligand charge transfer (MLCT) state energy, which is the lowest energy excited state for these complexes, is lowered upon chlorination of the terpyridyl ligand.

By performing simple PM3 semi-empirical calculations (Table S6, ESI)[†] on the free ligands, the authors found that the energies of the lowest-unoccupied molecular orbitals, LUMO and LUMO+1 for Cl-terpy and Cl₃-terpy are substantially lowered relative to those for terpy, despite their being little or no orbital contribution from the chlorine atoms. Contrastingly, the LUMO and LUMO + 1 energies of 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine, are raised due to their presence of electron-donating *tert*-butyl groups.

In an effort to gain further insight into how the ancillary substituents on the terpyridyl fragment can influence the HOMO and LUMO energies of the platinum(II) complexes, it was therefore necessary to assess the molecular structures and electronic properties of a series of platinum(II) terpyridyl complexes containing both electron-donating and electron-withdrawing substituents in the 4, 4' and 4"-positions of the terpyridyl backbone.

Minimum energy structures (full geometry optimizations) were calculated for [Pt(terpy)Cl]⁺ (**Pt1**) and a series of [Pt(4,4',4''-**R**₃-terpy)Cl]⁺ analogues (*where R is either an electron-donating* (*EDG*) or electron-withdrawing (*EWG*) group present in the ancillary positions) at the B3LYP/LACVP** level of theory. The calculated geometries are acceptable considering the degree of similarity between X-ray and DFT-calculated structures of the Pt-terpy analogues, *viz*. [Pt(terpy)(OMe)]⁺ and [Pt('Bu₃terpy)Cl]⁺.^{23,32} The calculated and observed bond distances and angles were in agreement to within 0.07 Å (for correlation see Table S7, ESI).[†]

Table 2 summarizes the calculated bond distances, *viz*. Pt– Cl, Pt–*trans*-N and Pt–*cis*-N, energies of the frontier molecular orbitals and electron densities surrounding the Pt(II) and Cl centres for each of the investigated derivatives, including **Pt1** and **Pt2**.

From Table 2it can be seen that, in terms of structural differences, the introduction of either electron-donating or electronwithdrawing groups in the ancillary positions of the terpyridyl fragment has a negligible influence. The *cis* and *trans* Pt–N bonds remain relatively constant, irrespective of the ancillary substituent, whilst the Pt–Cl bond, relative to that of [Pt(terpy)Cl]⁺, is seen to lengthen upon the introduction of electron-donating groups; in contrast the introduction of electron-withdrawing groups leads to a slight shortening of the Pt–Cl bond. In all instances, the Pt–Cl bond lengths do not deviate by more than 0.01 Å from that of [Pt(terpy)Cl]⁺.

This observed deviation in the Pt–Cl bond length, due to the presence of either electron-donating or electron-withdrawing groups in the ancillary positions respectively, despite being so small, can be attributed to the *trans*-influence, which is the influence of a coordinated ligand on the strength of the metal– ligand bond *trans* to itself and is a static ground-state effect. Thus, in the case of electron-donating groups being present in the ancillary positions of the terpyridyl fragment, electron-donation by the group in the 4'-position into the pyridyl ring, will lead to increased electron-density along the *trans* axis towards the platinum(II) centre thus weakening the Pt–Cl bond as reflected by the lengthening of this bond in the ground state. In the case

	Electron donat	Electron donating groups (EDG)				Electron withdrawing groups (EWG)			
	$\overline{H_2N}$	MeO-	^t Bu–	HO–	H	Cl–	$CF_{3}-$	CN-	NO ₂ -
Bond Lengths/Å									
Pt-Cl	2.358	2.353	2.352	2.352	2.347	2.344	2.341	2.338	2.336
Pt-trans-N	1.967	1.969	1.963	1.966	1.966	1.966	1.964	1.965	1.964
Pt-cis-N	2.050	2.050	2.050	2.048	2.052	2.051	2.051	2.050	2.051
MO Energies/eV	*								
EHOMO	-8.48	-8.99	-8.96	-9.01	-9.45	-9.64	-9.91	-10.18	-10.34
ELUMO	-5.05	-5.54	-5.55	-5.61	-6.16	-6.43	-6.77	-7.23	-7.47
ΔE	3.43	3.45	3.41	3.40	3.29	3.21	3.14	2.95	2.87
NBO Charges									
Pt	0.7007	0.7168	0.7155	0.7131	0.7300	0.7368	0.7478	0.7569	0.7620
Cl	-0.2241	-0.2083	-0.2055	-0.2024	-0.1873	-0.1791	-0.1683	-0.1573	-0.1504

Table 2Computational analysis of $[Pt^{II}(4,4',4''-R_3-terpy)Cl]^+$ analogues containing electron-donating (R = 'Bu-, H_2N-, MeO-or HO-) and electron-withdrawing (R = Cl-, NO_2-, CF_3-or CN-) groups in the ancillary positions of the terpy fragment

of an electron-withdrawing groups being present, we find that the opposite occurs as reflected by the shortening of the Pt–Cl bond in the ground state. Since this effect is not mirrored by the reactivity of the metal centre, we can assume that in this instance, that this is a result of ground-state destabilization by the *trans*influence as opposed to transition-state stabilization by the *trans*effect.

We also find that the positive charge on the metal centre decreases upon the introduction of electron-donating groups to the terpy fragment but increases upon the introduction of electron-withdrawing groups. Comparable effects have been noted previously in similar systems¹⁷ and this is reflected by the reactivity of these systems.

It is immediately noticeable from Table 2, that significant differences result in the frontier molecular orbital energies and the NBO charges of Pt and Cl upon the introduction of either electron-donating or electron-withdrawing groups at the 4, 4' and 4" positions. When considering the HOMO and LUMO energies, we see that compared to those of [Pt(terpy)Cl]⁺, the MO energies of the analogues containing electron-donating groups are higher, whilst those containing electron-withdrawing groups are comparably lower.

Subsequently, we also observe an increase in the energy separation of frontier molecular orbitals, ($\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$), upon the introduction of electron-donating groups and a corresponding decrease in ΔE in the case of electron-withdrawing groups being introduced. This is in correlation with what has been observed earlier for the free ligands by Cummings *et al.*³⁹

From the DFT-calculated ground state orbitals illustrated in Table 3, we find that in the case of electron-donating groups being present in the ancillary positions, the electron density of the HOMO is centred above and below the metal centre and towards the ancillary substituent, primarily along the *trans* axis, leading to a less electrophilic metal centre. In the case of electron-withdrawing groups being present, the electron density of the HOMO about the metal centre is significantly reduced, or absent as observed in the case of the substituent being the nitro $(-NO_2)$ group, and is located more on the ligand rendering the metal centre more electrophilic.

Indeed, based on the HOMO electron-densities, it would appear that the overall π *cis*-effect is greater than the overall π *trans*-effect for these systems. This correlates well with the work by Van Eldik *et al.*^{17,18} who found that π *cis*-effect is greater than the π *trans*-effect when dealing with platinum(II) complexes containing ligands with significant π -acceptor properties.

It can also be observed from the data in Table 2 that the magnitude of the values of E_{HOMO} , E_{LUMO} , ΔE and the NBO charges, is dependent upon the relative strength of the

electron-donating or -withdrawing groups and also the manner in which they function.

The manner in which some atoms or groups can withdraw or donate electrons into a system can be through either inductive (movement of electron density through σ -bonds) or resonance (movement of electron density through π -bonds) effects or a combination of the two.^{40,41}

From these, there are six possible combinations in which electron-density distribution in a system can be achieved:⁴⁰

(1) Groups that *withdraw* electrons by inductive effects only, *e.g.* $-CF_3$, $-NH_3^+$.

(2) Groups that *donate* electrons by inductive effects only, *e.g.* –CH₃, –CH₂CH₃, –CH(CH₃)₂.

(3) Groups that *withdraw* electrons through resonance only, *e.g.* –CN, –COH, –CO₂R (where R is any alkyl group).

(4) Groups that *withdraw* electrons both inductively and through resonance, *e.g.* –NO₂.

(5) Groups that withdraw electrons inductively **but** donate electrons through resonance *e.g.* -OH, $-NH_2$, -X (where X is a halide moiety).

(6) Groups that can *withdraw* or *donate* electrons through resonance, *e.g.* -Ph, $-CHCH_2$.

From the combinations given, it can be clearly seen how the ancillary groups chosen for the computational study function and allows us to explain in detail the trends observed.

In the case of the electron-withdrawing groups, the trend observed from the computed data correlates well with those in literature. Groups such as the cyano (–CN) or nitro (–NO₂) groups, are known to strongly withdraw electron-density^{40,41} and the presence of these in the ancillary positions of the terpyridyl fragment leads to greatest decrease in ΔE and also the greater positive charge on the metal centre when compared to [Pt(terpy)Cl]⁺.

The fact that these effects are slightly more pronounced for the nitro group than for the cyano group can be explained by considering the combinations give above, in which the nitro groups withdraws electron-density by both inductive and resonance effects, whereas the cyano group is only electron-withdrawing through resonance effects.

In the case of the electron-withdrawing substituent being the chloro (–Cl) moiety, the values obtained are slightly less than those for cyano or nitro, since halide ions are considered to be weaker electron-withdrawing groups as a result of them withdrawing electrons inductively *but* donating electrons through resonance. However the electron-withdrawing ability, as a result of the electronegativity of chlorine, is greater than its electron-donating ability, due to poorer overlap of the 3porbital of chlorine with the 2p orbital of the carbon it is attached to.

In the case of the amino $(-NH_2)$, methoxy (-OMe) and hydroxy (-OH) groups, we find that these operate *anti* to the chloride group in that they donate more electron-density through resonance effects than they accept electron-density through inductive effects. This is anticipated as a result of the lone pairs of electrons present in these groups being in close proximity to the extended π -conjugation of the terpyridyl fragment allowing for greater delocalization into the pyridyl rings. The *tert*-butyl group also functions as an electron-donating group, but primarily through inductive effects, with increased branching in the alkyl group leading to better electron-donating properties.

Conclusions

From the experimental data obtained, we find that the rate of substitution of the chloride moiety by the selected nucleophiles from **Pt2** proceeds at a slower rate than that from **Pt1**. This retardation in the rate of substitution has been attributed to the presence of the electron-donating substituents in the ancillary positions of the terpyridyl ligand in **Pt2** which leads to a reduction in the π -acceptor properties of the terpyridyl ring and subsequently a less electropositive metal centre.

The experimental and computational results clearly illustrate that the moderate decrease in reactivity of the metal centre upon introduction of electron-donating groups is as a result of a decrease in the positive charge of the metal centre and a corresponding increase in the energy separation of the frontier molecular orbitals (ΔE).

The introduction of electron-withdrawing groups leads to an increase in the positive charge of the metal centre and corresponding decrease in ΔE and should result in increased reactivity of the metal centre. By placing these ancillary substituents in both the *cis* and *trans* positions, we find that (i) the overall *trans*-influence is greater than the overall *trans*-effect; and (ii) the overall π *cis*-effect is greater than the overall π *trans*-effect. The strength of the electron-donating or -withdrawing groups controls the overall extent of π backdonation from the metal centre into the empty ligand orbitals.

The current study thus consolidates the role of electrondonating and electron-withdrawing groups in controlling the reactivity of platinum(II) terpyridyl complexes.

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