# To What Extent can the Pt–C Bond of a Metallacycle Labilize the *trans* Position? A Temperature- and Pressure-dependent Mechanistic Study†

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The orthoplatinated complex $[Pt\{C_6H_3X(CH_2NMe_2)\}(NC_5H_4SO_3\text{-}3)(H_2O)]$ (X = H **1a** or 3-MeO **1b**) was designed for mechanistic studies in water. The aqua ligand is located *trans* to the Pt–C bond of the phenyl group which lies in the platinum(II) co-ordination plane. The rates of substitution of the aqua ligand by a series of nucleophiles (Nu) ($Cl^-$, $Br^-$, $I^-$, $N_3^-$, $SCN^-$, thiourea, *N,N'*-dimethylthiourea or *N,N,N',N'*-tetramethylthiourea) were studied as a function of concentration, pH, temperature, and pressure by using a stopped-flow technique. The $pK_a$ value of the aqua ligand in **1a** is 9.75 ± 0.05 and the observed pseudo-first-order rate constants for the substitution reaction are given by $k_{obs} = k_1[Nu] + k_{-1}$. The $k_{-1}$ term arises from the reverse solvolysis reaction and is insignificant for stronger, S-donor nucleophiles. The values of $k_1$ are *ca.* four orders of magnitude higher than the corresponding rate constants for anation reactions of $[Pt(dien)(H_2O)]^{2+}$ (dien = diethylenetriamine) and close to the rate constants for anation of $[Pd(dien)(H_2O)]^{2+}$. The effect is largely due to a strong decrease in $\Delta H^‡$. An analysis of the activation parameters, $\Delta H^‡$, $\Delta S^‡$ and $\Delta V^‡$, clearly shows that the substantial rate increase is not associated with a changeover in mechanism and that the substitution process is still associative in nature.

In most textbooks dealing with inorganic reaction mechanisms[1–4] the rates of water exchange on aquated metal ions are used to demonstrate that the reactivity of many platinum(II) complexes is a factor of $10^5$–$10^6$ lower than that of the corresponding palladium(II) complexes. This reactivity difference can strongly depend on the co-ordination environment, as well as on the nature of the entering and leaving ligands. Earlier work by Basolo *et al.*[5] and Romeo and co-workers[6–8] has demonstrated how the introduction of a metal–carbon bond can substantially labilize the *trans* position for substitution reactions in non-aqueous media. The large reactivity difference found for the exchange of O- and N-donor ligands on platinum(II) and palladium(II) centres almost disappears on the introduction of four metal–carbon bonds.[9]

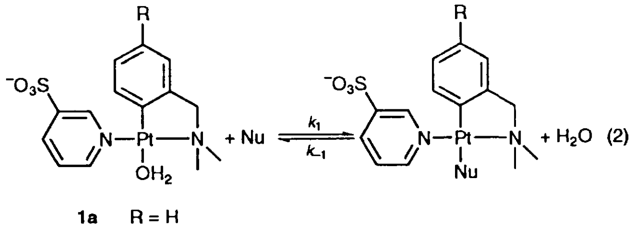
Recently, Romeo *et al.*[10,11] analysed the factors that could cause a mechanistic changeover from associative to dissociative ligand-substitution reactions in complexes of the type *cis*-$[PtR_2(Et_2S)_2]$ (R = Me or Ph), *i.e.* species containing two Pt–C bonds. The reasons for the changeover is a combination of ground-state labilization and the increased electron density at the metal centre which inhibits the nucleophilic attack of incoming ligands. In contrast, however, the complex *cis*-$[PtPh_2(CO)(Et_2S)]$ does not show the mechanistic changeover and the offered explanation calls for further investigations.[11]

In a series of studies[12–14] we have demonstrated that the reactivity of $[PdL(X)]^+$ complexes [L = pentaalkyl-substituted derivatives of diethylenetriamine (dien)], in the substitution reaction (1), M = Pd, can be significantly reduced by

$$[ML(H_2O)]^{2+} + X^{n-} \rightleftharpoons [ML(X)]^{(2-n)+} + H_2O \quad (1)$$

the introduction of steric hindrance such that it attains the level typical of the unsubstituted $[Pt(dien)X]^{(2-n)+}$ complexes. Obviously, it is easier to decrease the reactivity by steric hindrance than to increase it to a similar degree by, for instance, electronic effects. In principle this should be possible *via* the introduction of a metal–carbon σ bond.

Analysis of X-ray structural data has demonstrated[15] that the M–C bond in square-planar aryl complexes is shortest when the aryl group lies in the metal plane. Therefore, such aryl groups must affect the reactivity most. One way to bring about the required ligand arrangement is *via* orthometallation. The chemistry of orthometallated transition-metal complexes has been an area of active research in recent years,[16] providing a wide choice of synthetic procedures. For our study, we have prepared the orthoplatinated derivatives of *N,N*-dimethylbenzylamine of type **1** and measured the rates of a series of ligand-substitution reactions (2) (Nu = nucleophile) as a function of concentration, pH, temperature and pressure in aqueous solution. A preliminary account of this work has appeared,[17] and details of a more complete study are reported here. Surprisingly, the introduction of the metal–carbon σ bond does not cause a changeover in mechanism, although it increases the lability of the complex by four orders of magnitude. The analogous palladium(II) complex was also synthesised. Complex-formation reactions with chloride were too fast for stopped-flow techniques, and could therefore not be investigated.



**1a** R = H
**1b** R = OMe

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† *Supplementary data available* (No. SUP 56997, 13 pp.): preparative details and observed and calculated rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

## Experimental

*General.*—Spectrophotometric measurements were performed on a Cary 1 (Varian) spectrophotometer. Proton NMR spectra were run on a AM 400 WB Bruker instrument. Chemical shifts are in δ throughout. The Fourier-transform IR spectra of solid compounds were recorded in KBr discs by using a Nicolet 5 SX spectrophotometer. The kinetics of the ligand-substitution reactions was studied on a Dionex D110 stopped-flow instrument, thermostatted to within ±0.1 °C, at ambient pressure. Experiments at elevated pressure (up to 150 MPa) were performed on a laboratory-made high pressure stopped-flow instrument.[18] Kinetic traces were analysed by using the OLIS KINFIT (On-Line Instrument Systems, Bogart, USA) set of programs. Analytical data were obtained from Beller Analytisches Laboratorium (Göttingen). Melting points were determined with the help of a Digital Melting Point Apparatus and are uncorrected.

*Chemicals and Ligands.*—*N*,*N*-Dimethylbenzylamine and 3-methoxy-*N*,*N*-dimethylbenzylamine were obtained from Aldrich and the former was distilled before use. All other chemicals were of p.a. quality and used without further purification. The chemicals were obtained from Merck [NaCl, NaBr, NaI, $NaN_3$, thiourea (tu), $NaClO_4$], J. J. Baker (NaSCN), EGA [*N*,*N*′-dimethylthiourea (dmtu)] and Janssen [*N*,*N*,*N*′,*N*′-tetramethylthiourea (tmtu)].

*Platinum*(II) *Complexes* **1a** *and* **1b**.—The chloro-bridged dimeric precursors $[\{Pt[C_6H_3X(CH_2NMe_2)]Cl\}_2]$ (X = H or 3-MeO) of the complexes **1a** and **1b** were prepared using essentially the procedure described in the literature.[19] The minor differences are described elsewhere.[20] These were converted into the monomeric species **1a** and **1b** as follows. To a suspension of $[\{Pt(C_6H_4CH_2NMe_2)Cl\}_2]$ (0.15 g, 0.2 mmol) in water (150 $cm^3$), pyridine-3-sulfonic acid (Aldrich) (0.072 g, 0.45 mmol) was added and the mixture was stirred for 2 d using a magnetic bar at *ca.* 50 °C. The conversion of the pale yellow hydrophobic powder of the chloro-bridged dimer into a snow-like white precipitate indicated that monomerization/hydrolysis had occurred. The compound formed was filtered off, washed with a small amount of cold water to remove traces of the pyridine ligand and dried in air. Finally, the product was washed with $CH_2Cl_2$ to separate it from the unreacted dimer. Drying in air provided the analytically pure material. Yield 0.134 g (62%) (Found: C, 33.25; H, 3.60; Cl, < 0.1; Pt, 38.60. Calc. for $C_{14}H_{18}N_2O_4PtS$: C, 33.30; H, 3.40; Pt, 38.55%). M.p. 314 °C (decomp.). $^1H$ NMR [$(CD_3)_2SO$]: δ 3.32 (br s, $NCH_3$), 4.07 (br s, $NCH_2$), 5.85 (br, $H^6$), 6.74 (t, $H^4$), 6.97 (br, $H^5$), 7.06 (br, $H^3$), 7.69 (t, $H^{5'}$), 8.29 (d, $H^{4'}$), 8.94 (d, $H^{6'}$) and 9.10 (s, $H^{2'}$). IR: 1263 and 1170 $cm^{-1}$ ($SO_3^-$). Complex **1b** was prepared and characterized similarly.

## Results

*Synthesis of the Starting Platinacycles* **1** *and their Precursors.*—Preparation of cyclometallated platinum(II) complexes *via* C–H bond activation is more complicated than for the palladium(II) analogue.[16] Therefore, a few attempts were made to increase the yield of the chloro-bridged precursors of **1** starting from *N*,*N*-dimethylbenzylamines and $[PtCl_4]^{2-}$ on the basis of the current knowledge on the mechanism of cyclometallation.[21] In the case of $Pd^{II}$ the yields are increased by the presence of base, $NaO_2CMe$ in particular.[22] However, addition of this salt to the system $K_2[PtCl_4]$–$PhCH_2NMe_2$–water–MeOH resulted in only Pt metal. When $[NH_4]_2[PtCl_4]$ was used instead of the potassium salt, pink crystals of $[PhCH_2NHMe_2]_2[PtCl_4]$ were first formed [equation (3)] followed by a build-up of cisplatin [equations (4) and (5)]. No

$$2\,PhCH_2NMe_2 + [NH_4]_2[PtCl_4] \rightleftharpoons [PhCH_2NHMe_2]_2[PtCl_4] + 2\,NH_3 \quad (3)$$

$$[NH_4]_2[PtCl_4] + 2\,NH_3 \rightleftharpoons cis\text{-}[Pt(NH_3)_2Cl_2] + 2\,NH_4Cl \quad (4)$$

$$[PhCH_2NHMe_2]_2[PtCl_4] + 2\,NH_3 \rightleftharpoons cis\text{-}[Pt(NH_3)_2Cl_2] + 2[PhCH_2NHMe_2]Cl \quad (5)$$

formation of orthoplatinated species was observed in this system. Orthometallation of $[PhCH_2NHMe_2]_2[PtCl_4]$ in dimethylformamide (dmf) in the presence of $K_2CO_3$, as described by Newkome *et al.*,[23] resulted in only a 10% yield (SUP 56997). Thus, we failed to increase the yield by using procedures other than those put forward by Cope and Friedrich.[19] The old method still remains the best although the overall yield does not exceed 28%.

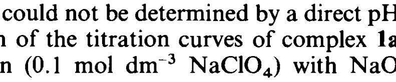
The monomerization of $[\{Pt[C_6H_3X(CH_2NMe_2)]Cl\}_2]$ by pyridine-3-sulfonic acid, which was selected to improve the water solubility of the products, proved to be rather difficult because of the antagonistic solubility of the reactants in common solvents. As a result, the reaction which proceeds according to equation (6) was carried out in water under

$$[\{Pt[C_6H_3X(CH_2NMe_2)]Cl\}_2] + 2\,NC_5H_4SO_3H\text{-}3 \longrightarrow 2\,\mathbf{1} + 2\,HCl \quad (6)$$

heterogeneous conditions. A remarkable feature of this process is that it is accompanied by hydrolysis of the chloro ligand. Chloride normally remains bound to monomeric platinacycles of this type, and the observed hydrolysis is a first manifestation that the position *trans* to the Pt–C bond has in fact been labilized. Proton NMR data for complexes **1** are in full accord with the proposed structure and clearly show that the phenyl ring is *trans* to the aqua ligand, since the proton $H^6$ of the orthoplatinated ring is strongly shifted upfield.[16] The sulfonic group of co-ordinated pyridine is deprotonated as suggested by the observation that the pH of aqueous solutions of **1a** is neutral. Thus, complexes **1** are formally uncharged and possess a zwitterionic character.[24] As a result, their aqueous solubility, although sufficient for spectrophotometric studies, is lower than we actually anticipated.

*Thermodynamic Studies of Complexes* **1** *in Water.*—*Preparation of complex solutions.* Aqueous solutions of complex **1a** were prepared by dissolving it in 0.1 mol $dm^{-3}$ $NaClO_4$ the pH of which was adjusted to 4 with diluted $HClO_4$. The maximum solubility of the complex is about 2 × $10^{-4}$ mol $dm^{-3}$. Complex **1b** is insoluble in water. Therefore it was first dissolved in dmf and then an aqueous 0.1 mol $dm^{-3}$ $NaClO_4$ solution was added. It was checked with **1a** that addition of up to 10% dmf did not influence the kinetic behaviour. This indicates that the aqua complex is the reactive species under our conditions.

*Acidity and complex formation.* Owing to the low solubility, the p$K_a$ value could not be determined by a direct pH titration. A comparison of the titration curves of complex **1a** and of a blank solution (0.1 mol $dm^{-3}$ $NaClO_4$) with NaOH clearly showed that there is an acidic equivalent and the p$K_a$ value [equation (7)] was expected to be in the range 9–10. Aqueous



(7)

solutions of **1a** are characterized by an absorption maximum at 247 nm at pH ⩽8.3 and at 267 nm at pH ⩾11.5 with an isosbestic point at 261 nm. Plots of absorbance *vs.* pH allow the determination of the p$K_a$ of co-ordinated water. Fig. 1 shows this plot for measurements at 280 and 290 nm and a non-linear least-squares fit of the data gives values of 9.76 ± 0.05 and 9.73 ± 0.05 for the p$K_a$, respectively. The Lambert–Beer law holds for concentrations up to 2 × $10^{-4}$ mol $dm^{-3}$ ruling out aggregation or dissociation of the pyridine ligand in this concentration range.

Addition of nucleophiles to solutions of complex **1a** at pH *ca.* 4 shifts the absorbance maximum to higher wavelengths and isosbestic points are observed at 252 nm for $Cl^-$ and $Br^-$, suggesting a 1 : 1 complex formation according to equation (2). A representative plot of absorbance at a fixed wavelength *versus* ligand concentration is shown in Fig. 2 which can be expressed in the form of equation (8), where $A_0$ and $A$ are absorbances in

$$(A - A_0)/[Nu] = K_1A_\infty - K_1A \qquad (8)$$

the absence and in the presence of added nucleophile Nu, respectively, and $A_\infty$ is the absorbance at infinite concentration of Nu, resulting in the equilibrium constants $K_1$ summarized in Table 1. A first remarkable feature of this system can be seen if the value of $K_1$ for $Cl^-$ is compared to the corresponding equilibrium constant for $[Pt(dien)H_2O]^{2+}$, $3 \times 10^3$ $dm^3$ $mol^{-1}$.[25] The difference of a factor of 33 clearly shows a significantly reduced preference of **1a** for the chloride ligand.

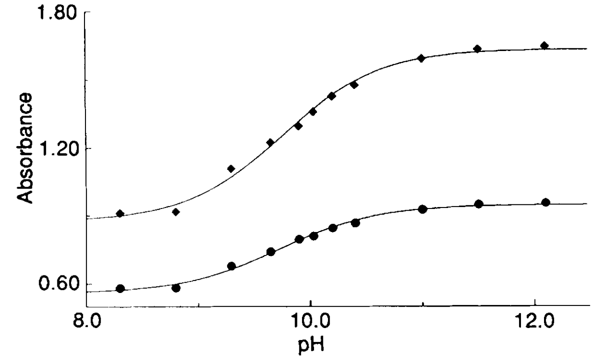


**Fig. 1** Dependence of the absorbance of complex **1a** on pH at 25 °C, $[NaClO_4] = 0.1$ mol $dm^{-3}$, $[Pt] = 2 \times 10^{-4}$ mol $dm^{-3}$, optical pathlength = 1 cm; λ = 280 (◆) or 290 nm (●)

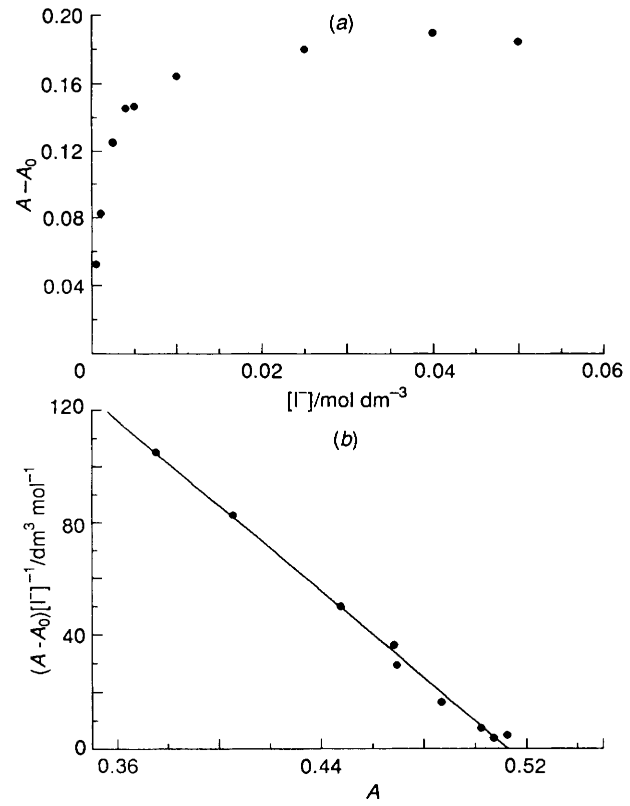


**Fig. 2** Determination of the equilibrium constant for reaction (2) with iodide as entering nucleophile; (*a*) plot of absorbance at 280 nm *versus* $[I^-]$; (*b*) plot of $(A - A_0)/[I^-]$ *versus* $A$ for the data in (*a*). Conditions: optical pathlength = 0.88 cm, 25 °C, $[NaClO_4] = 0.1$ mol $dm^{-3}$, $[Pt] = 5 \times 10^{-5}$ mol $dm^{-3}$, pH 4

*Kinetics of Reactions with Nucleophiles.—Influence of ligand concentration.* The kinetics of reaction (2) was followed spectrophotometrically for a variety of incoming ligands of different nucleophilicity in the temperature range 14.1–43.7 °C, mostly at pH *ca.* 4, where complexes **1** exist in the aqua form. A stopped-flow technique was used to measure the absorbance increase due to the formation of the ligated species. All measurements were performed in an excess of the incoming ligands to ensure pseudo-first-order conditions. Pseudo-first-order rate constants, $k_{obs}$, were calculated from the kinetic traces and plotted against the concentration of the incoming nucleophiles. The plots obtained were similar for all cases studied and representative cases are shown in Fig. 3. It follows that $k_{obs}$ can be expressed by equation (9) and the calculated

$$k_{obs} = k_1[Nu] + k_{-1} \qquad (9)$$

values of $k_1$ and $k_{-1}$ are summarized in Table 2 along with the associated activation parameters, $\Delta H^‡$ and $\Delta S^‡$, which were calculated from the temperature dependencies of the rate constants. For the most reactive ligands no noticeable intercepts were observed, *i.e.* $k_{-1} \approx 0$. In those cases where the intercepts could be evaluated quite reliably, the ratios $k_1/k_{-1}$ were calculated and compared with the equilibrium constants $K_1$ measured spectrophotometrically (see Table 1). The acceptable agreement between the thermodynamically and kinetically determined equilibrium constants demonstrates that the system under study can be described by equation (2). A subsequent, second reaction step was observed only in the case of $SCN^-$ as entering nucleophile, for which $k_{obs}$ was independent of the $SCN^-$ concentration. This is presumably due to an intramolecular linkage isomerization.

*Effect of* pH. Our earlier work on the substitution mechanisms of square-planar complexes[26,27] clearly demonstrated that co-ordinated water is very labile and easily

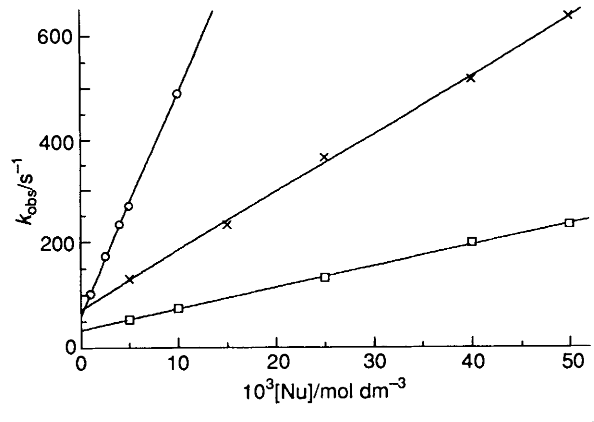


**Fig. 3** Examples of the dependence of $k_{obs}$ on the concentration of the incoming nucleophile at 25 °C, $[NaClO_4] = 0.1$ mol $dm^{-3}$, pH 4. Nucleophile (Nu) = $Cl^-$ (□), $Br^-$ (×) or $I^-$ (○)

**Table 1** Equilibrium constants $K_1$ obtained from UV/VIS measurements and calculated from the kinetic data $(k_1/k_{-1})$ at 25 °C, ionic strength 0.1 mol $dm^{-3}$ $(NaClO_4)$ and pH 4

| Nucleophile | $k_1(k_{-1})^{-1}/dm^3\ mol^{-1}$ | $K_1/dm^3\ mol^{-1}$ |
|---|---|---|
| $Cl^-$ | 117 ± 9 | 90 ± 16 |
| $Br^-$ | 159 ± 19 | 141 ± 9 |
| $I^-$ | 730 ± 50 | 760 ± 20 |
| $N_3^-$ | 3200 ± 960 | 3170 ± 120 |

substituted on palladium(II) and platinum(II) centres. However, when the aqua ligand is deprotonated to produce the hydroxo species, the inertness of the complex increases drastically and in many cases the substitution is not observed at all. The same behaviour was anticipated for the present system and a typical pH profile for the reaction of **1a** with thiourea is presented in Fig. 4. The reaction rate is pH-independent in the range 4–8 but is practically zero at pH 12. This dependence is obviously described by equation (10) and the p$K_a$ value obtained by fitting

$$k_{obs} = \frac{k_1[H^+][Nu]}{K_a + [H^+]} \qquad (10)$$

the experimental data by this equation equals 9.7 ± 0.1. This value is in excellent agreement with that obtained from the spectrophotometric experiments. Rather surprisingly, it is considerably higher than the 4.18 which was found[28] for the palladium complex $[Pd(C_6H_4CH_2NMe_2)(py)(H_2O)]^+$ (py = pyridine). The difference may partly be understood by taking into account that the platinum complex is neutral, whereas the palladium complex has a +1 charge, thus a lower p$K_a$ is to be expected.[29] However, the observed difference seems to be too large to be solely due to charge effects.

*Pressure effects.* These have been studied for azide and tmtu as incoming ligands. In the former case, the effect of pressure on both the forward ($k_1$) and reverse ($k_{-1}$) reactions was investigated, and this allows one to construct a volume profile for the reaction. The data obtained, Fig. 5, show that the reactions are accelerated by pressure, which is indicative of an associative substitution mechanism. The volumes of activation, $\Delta V^‡$, calculated from the data in Fig. 5 are summarized in Table 3.

*Subtuning of the reactivity.* As we will discuss in more detail below, we have been able *substantially* to increase the reactivity of platinum(II) complexes on the basis of the orthometallation concept. It was further interesting to investigate the possibility of 'subtuning'. For instance, will electron-donating groups attached to the platinum-bound phenyl ring in complexes **1** also increase the substitution rate? We have therefore studied the rate of the reaction between **1b** and iodide at 25 °C, pH *ca.* 4 and 0.1 mol dm$^{-3}$ $NaClO_4$. As could be expected, the presence of a methoxy group in **1b** does not change the rate equation (9) but does affect the rate constants $k_1$ and $k_{-1}$ and they differ from those for **1a** (Table 2). Interestingly, the electron-donating group decreases the $k_1$ value by a factor of two, which is probably related to specific back-bonding effects (see Discussion).

*Influence of chloride.* By way of comparison, the substitution reactions of aqua complexes are usually orders of magnitude faster than those of the corresponding chloro complexes,[30] such that chloride can be an efficient competitor during such

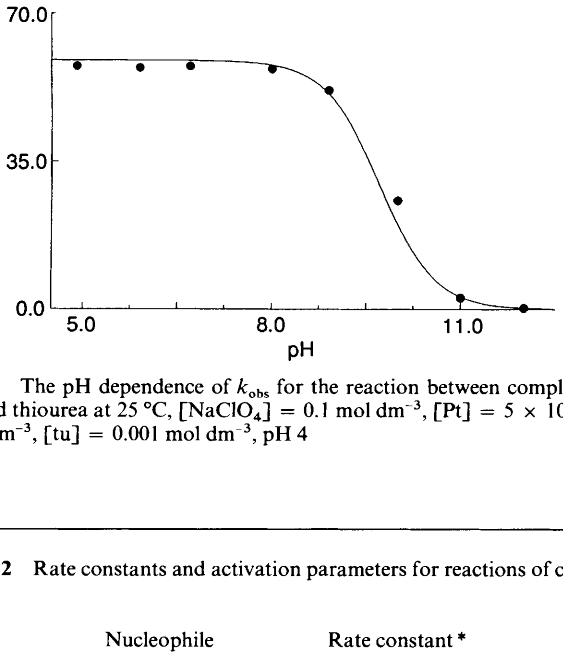


**Fig. 4** The pH dependence of $k_{obs}$ for the reaction between complex **1a** and thiourea at 25 °C, $[NaClO_4]$ = 0.1 mol dm$^{-3}$, [Pt] = 5 × 10$^{-5}$ mol dm$^{-3}$, [tu] = 0.001 mol dm$^{-3}$, pH 4

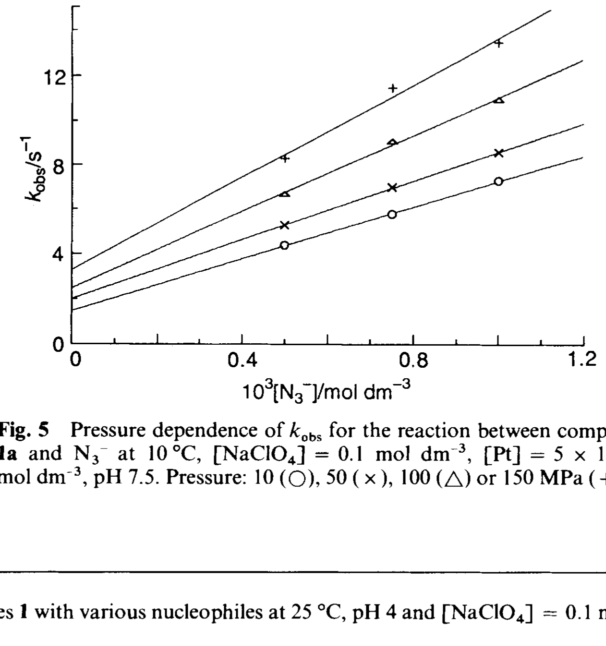


**Fig. 5** Pressure dependence of $k_{obs}$ for the reaction between complex **1a** and $N_3^-$ at 10 °C, $[NaClO_4]$ = 0.1 mol dm$^{-3}$, [Pt] = 5 × 10$^{-5}$ mol dm$^{-3}$, pH 7.5. Pressure: 10 (○), 50 (×), 100 (△) or 150 MPa (+)

**Table 2** Rate constants and activation parameters for reactions of complexes **1** with various nucleophiles at 25 °C, pH 4 and $[NaClO_4]$ = 0.1 mol dm$^{-3}$

| Nucleophile | Rate constant * | | $\Delta H^‡$/kJ mol$^{-1}$ | $\Delta S^‡$/JK$^{-1}$mol$^{-1}$ |
|---|---|---|---|---|
| (*a*) Complex **1a** | | | | |
| $Cl^-$ | $k_1$ | 4 000 ± 75 | 30.3 ± 3.0 | −74 ± 10 |
| | $k_{-1}$ | 34 ± 2 | 47.5 ± 5.4 | −56 ± 18 |
| $Br^-$ | $k_1$ | 11 300 ± 230 | 25.1 ± 0.7 | −83 ± 2 |
| | $k_{-1}$ | 71 ± 7 | 50.3 ± 1.5 | −41 ± 5 |
| $I^-$ | $k_1$ | 42 900 ± 520 | 27.6 ± 2.2 | −63 ± 6 |
| | $k_{-1}$ | 59 ± 3 | 38.7 ± 1.3 | −82 ± 4 |
| $N_3^-$ | $k_1$ | 15 200 ± 180 | 25.6 ± 0.8 | −79 ± 3 |
| | $k_{-1}$ | 4.8 ± 1.8 | 43.8 ± 2.0 | −85 ± 6 |
| $SCN^-$ | $k_1$ | 40 700 ± 740 | 16.9 ± 0.3 | −100 ± 1 |
| tu | $k_1$ | 55 000 ± 400 | 20.9 ± 0.8 | −84 ± 3 |
| dmtu | $k_1$ | 57 700 ± 400 | 22.0 ± 0.6 | −80 ± 2 |
| tmtu | $k_1$ | 16 800 ± 240 | 31.8 ± 1.2 | −57 ± 4 |
| (*b*) Complex **1b** | | | | |
| $I^-$ | $k_1$ | 21 000 ± 3000 | | |
| | $k_{-1}$ | 55.5 ± 0.9 | | |

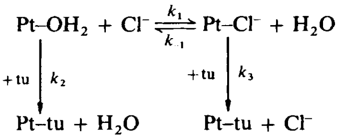
* $k_1$ is in dm$^3$ mol$^{-1}$ s$^{-1}$; $k_{-1}$ in s$^{-1}$.

**Table 3** Activation volumes for reactions of complex **1a** with azide and tetramethylthiourea

| Nucleophile | Rate constant | $T/^{\circ}C$ | $\Delta V^{\ddagger}/cm^3\ mol^{-1}$ |
|---|---|---|---|
| $N_3$ | $k_1$ | 10 | $-10.1 \pm 0.6$ |
| $N_3^-$ | $k_{-1}$ | 10 | $-12.4 \pm 0.9$ |
| tmtu | $k_1$ | 25 | $-10.5 \pm 0.1$ |

reactions. This aspect is especially of biological interest and for that reason the influence of chloride on substitution reactions of $[PdL(H_2O)]^{2+}$ and $[PdL(H_2O)_2]^{2+}$ (L = pentasubstituted dien or tetrasubstituted ethylenediamine) have been studied in the past.[31,32] A series of experiments were therefore performed to investigate the influence of chloride on the substitution behaviour of **1a**.

In the first experiments the aqua complex was treated with a mixture of $Cl^-$ and thiourea. The observed kinetic traces resulted in rate constants in good agreement with the sum of the rate constants for the two parallel reactions. In the second series of experiments chloride was added to the aqua complex prior to addition of tu, and the data are summarized as a function of $[Cl^-]$ and [tu] in Fig. 6. Enlargement of the lower concentration range [Fig. 6(*b*)] clearly shows that the plot of $k_{obs}$ *versus* [tu] is significantly curved and decreases with increasing $[Cl^-]$. At higher [tu] the data seem to fall all on one line within the experimental error limits. The mechanism in Scheme 1 can account for these data when a direct reaction of the chloro complex with tu is included. Under steady-state conditions equation (11) describes the concentration dependence of $k_{obs}$, according to which plots of $k_{obs}$ *versus* [tu] should be curved at low [tu] and become linear at high [tu], where equation (11)



**Scheme 1**

$$k_{obs} = \frac{k_{-1}k_2[tu]}{k_1[Cl^-] + k_2[tu]} + k_3[tu] \qquad (11)$$

simplifies to $k_{obs} = k_{-1} + k_3[tu]$. These trends are in good agreement with the data reported in Fig. 6 and those found for related systems.[33]

A non-linear least-squares fit for all the data in Fig. 6 showed that $k_1$ and $k_2$ are interdependent. By taking the value reported in Table 2 for one of them, the fit resulted in $k_3 = 1950 \pm 150$ $dm^3\ mol^{-1}\ s^{-1}$ and values for the other two constants in close agreement with those in Table 2. Alternatively, the data at [tu] $\geqslant 0.01$ mol $dm^{-3}$ can be fitted with the linear form of equation (11) and result in $k_3 = 1850 \pm 120$ $dm^3\ mol^{-1}\ s^{-1}$ and $k_{-1} = 36 \pm 4\ s^{-1}$. The latter value is once again in good agreement with that in Table 2. The values of $k_3$ indicate that the reaction of the chloro complex with tu is *ca.* 30 times slower than the corresponding reaction of the aqua complex, in agreement with our expectations.

## Discussion

What could be achieved in this study? First, very high substitution rate constants $k_1$ for platinum(II) complexes **1** in reactions (2) were reached. It is clearly seen from Fig. 7, in which the corresponding reactivity of $[ML(H_2O)]^{2+}$ (M = Pd or Pt, L = pentasubstituted dien) complexes is compared to that of **1a**, that the latter complex reacts as fast as $[Pd(dien)(H_2O)]^{2+}$.

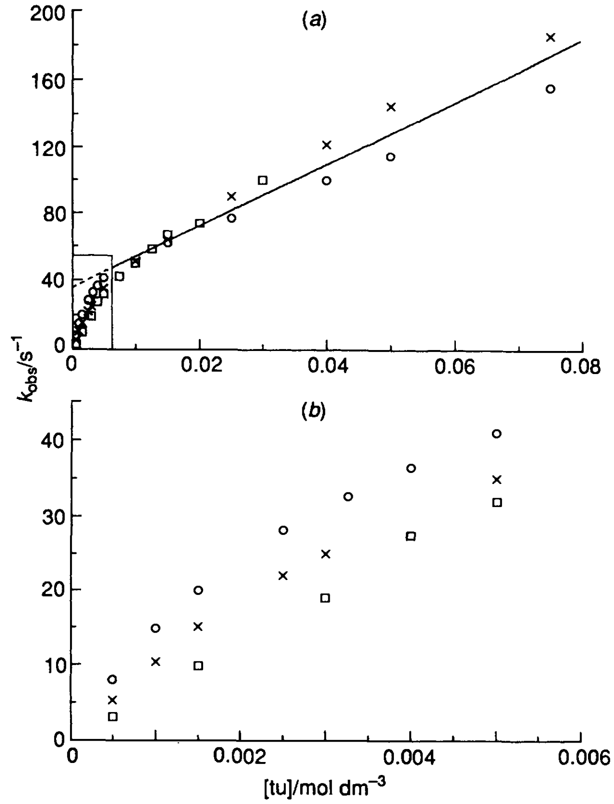


**Fig. 6** Influence of $[Cl^-]$ on $k_{obs}$ for the reaction of complex **1a** with tu at $[NaClO_4] = 0.1$ mol $dm^{-3}$, pH 4. See Discussion section. $[Cl^-] =$ 0.025 (○), 0.05 (×) or 0.1 mol $dm^{-3}$ (□)

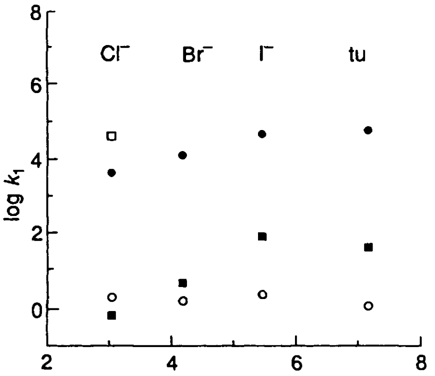


**Fig. 7** Dependence on the relative nucleophilicity, $n^0_{Pt}$ (ref. 1, p. 399), of the rate constants for anation[14] of complex **1a** (●), $[M(dien)(H_2O)]^{2+}$ [M = Pd (□) or Pt (■)] and $[PdL(H_2O)]^{2+}$ (○) with $Cl^-$, $Br^-$, $I^-$ and tu; L = $Et_2N(CH_2)_2NMe(CH_2)_2NEt_2$ for $Cl^-$, $Br^-$ and $I^-$ and $Et_2N(CH_2)_2NEt(CH_2)_2NEt_2$ for tu

Thus, our approach based on the introduction of an ortho-platinated backbone brought about a 'palladium' reactivity in the platinum complexes by increasing their reactivity by a factor of $10^4$–$10^5$. The major reason for the enhanced reactivity is a considerable lowering in the activation enthalpies, $\Delta H^{\ddagger}$. The activation parameters in Table 2 must be compared to those reported a decade ago by Romeo and Cusumano[34] for the forward path of reaction (1) with M = Pt, L = dien and X = $I^-$ or thiourea. For these two nucleophiles $\Delta H^{\ddagger}$ values of 42.7 and 41.4 kJ $mol^{-1}$ and $\Delta S^{\ddagger}$ values of −67 and −77 J $K^{-1}$ $mol^{-1}$, respectively, were reported. The change in $\Delta H^{\ddagger}$ is especially pronounced in the thiourea case, where we have achieved a two-fold decrease in $\Delta H^{\ddagger}$. It should be emphasized that the values of $\Delta S^{\ddagger}$ remained practically unaltered and are large and

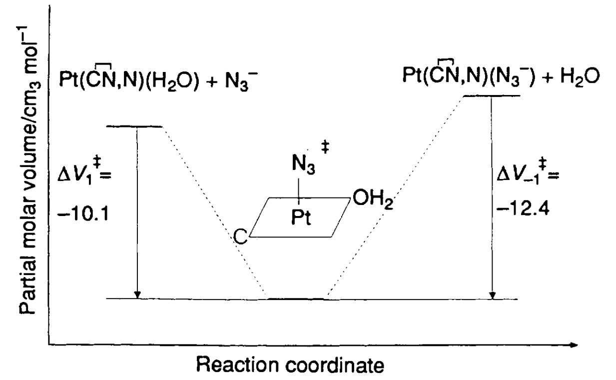


**Fig. 8** Volume profile for the reaction between complex **1a** and $N_3^-$ at $[NaClO_4] = 0.1$ mol dm$^{-3}$, 10 °C, [Pt] $= 5 \times 10^{-5}$ mol dm$^{-3}$, pH 7.5

negative, indicating that the mechanism remains associative in nature.

We were able to measure the pressure dependencies for the forward and reverse reactions in equation (2) for the case of complex **1a** and azide. The values of $\Delta V^{\ddagger}_1$ and $\Delta V^{\ddagger}_{-1}$ were used to construct a volume profile for this reaction which is shown in Fig. 8. It should be noted that the reverse reaction (2) is an aquation process, *i.e.* the interaction of the azide complex with a water molecule, since it is well documented that the rate of hydrolysis of such complexes is independent of $[OH^-]$.[35] This means that, even in basic solution, aquation is rate-determining followed by a rapid deprotonation step to produce the hydroxo complex. The $\Delta V^{\ddagger}_{-1}$ value of $-12.4 \pm 0.9$ cm$^3$ mol$^{-1}$ is very typical of that found for similar aquation reactions[26] in which an ionic ligand is replaced by a neutral solvent molecule, and characteristic for an associative substitution mechanism. Anation reactions are in general also characterized by significantly negative $\Delta V^{\ddagger}_1$ values,[26] although the intrinsic volume decrease due to bond formation is expected to be partially cancelled by a volume increase arising from charge neutralization when the entering nucleophile is an anionic species. For instance $\Delta V^{\ddagger}_1$ for anation of $[PdL(H_2O)]^{2+}$ (L = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) by $N_3^-$ was reported[36] to be $-11.7 \pm 1.2$ cm$^3$ mol$^{-1}$, which is remarkably close to the value found in the present study. All in all, the transition state has a significantly more compact structure than that of either the reactant or product states, demonstrating the importance of bond formation in both the forward and reverse reactions (2).

What could not be achieved in this study? The dramatic increase in the reactivity of the square-planar platinum(II) complexes did not bring about a changeover in the mechanism of substitution from associative, which is typical for square-planar systems,[37] to dissociative, which has become an attractive phenomenon to study.[8,10,11] The mechanism of the complex-formation reactions (2) remains associative and this is first of all seen from the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table 2). The former are much too low, whereas the latter are too negative to be associated with bond breaking in the transition state. The reported activation volumes (Table 3) provide further conclusive support. All the values are close to $-10$ cm$^3$ mol$^{-1}$ and these are very typical of associative substitution reactions in square-planar complexes of Pd and Pt.[26] A question that may be asked is whether it is, in principle, possible to observe the mechanistic changeover by increasing the reactivity electronically? Probably not, since we reached the reactivity level typical of palladium(II) complexes, but these, in turn, still react associatively! Complexes **1** are constructed such that there are no impediments for the axial attack by incoming ligands. We suspect that the most important prerequisite for dissociative activation in square-planar complexes is enhanced reactivity, on the one hand, and substantial retardation of the axial attack, either sterically or electronically, on the other. One can argue that at least in some platinum(II) systems, for which the dissociative mechanism has been put forward,[8,10] the approach to the axial sites could be hindered by *ortho* substituents or σ-bound phenyl groups. At present, only one thing seems absolutely clear: such substituents strongly decrease associative attack at platinum(II) complexes.[29]

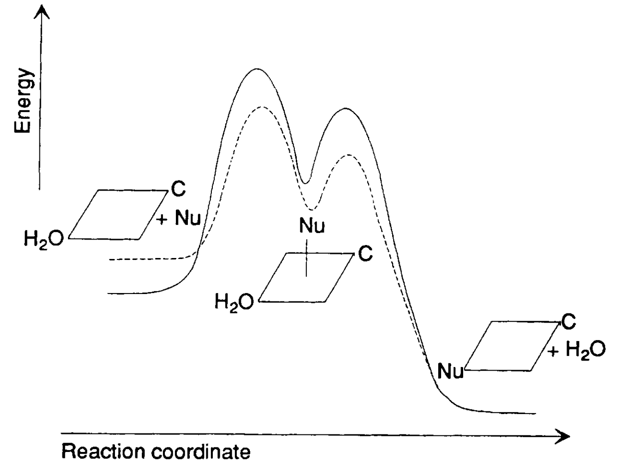


**Fig. 9** Energy profile for associative substitution at a square-planar metal centre. The dashed line shows how the orthoplatinated backbone may reduce the activation barrier; see text for details

An intriguing task is to account in a mechanistic sense for the rate acceleration. This will be done on the basis of the classical separated bond-making/bond-breaking treatment of square-planar substitution.[2] Since we never observed accumulation of a five-co-ordinated intermediate, the first energy barrier must be evidently higher and this must hold throughout this discussion. Obviously, the reaction rate will increase due to either destabilization of the ground state or stabilization of the transition state on introducing a M–C bond. One cannot exclude that the two effects play a simultaneous role (and this is most likely the case), but for the sake of clarity they will be considered separately. Ground-state destabilization does occur and this is manifested in significant elongation of the metal–halide bonds *trans* to the σ-bound carbon of the ortho-metallated ligands.[28] The same is probably also true for analogous $M–OH_2$ bonds, but such information is very scarce.[38] Naturally, the ground-state destabilization by itself could account for the observed effect. However, the structure of complexes **1** has additional intrinsic features that may provide the transition-state stabilization as well. The shortest aryl–metal bond observed when the aryl ligand and platinum metal comprise one and the same plane is evidently due to the back bonding from the $d_{xz}$ metal orbital into the aromatic antibonding π* orbital. Hence, there must be some flow of electron density away from the metal due to back donation. Consequently, it may favour axial nucleophilic attack and thus decrease the first energy barrier. The retardation effect of the methoxy group is in qualitative accord with this proposal. However, in order to keep the observed reactivity the same, *i.e.* without the accumulation of a five-co-ordinated intermediate,[39] the second barrier should also be lowered. This is an area where the Pt–C bond can be manifested by labilizing the *trans* co-ordination position. Therefore, the orthoplatinated ligand can, in principle, transform the (solid) energy profile for the anation reaction in Fig. 9 into the dashed one and thus enhance the square-planar substitution process.

## Conclusion

We have shown that it is possible to tune the reactivity of different metal centres by introducing palladium(II) substitution rates for orthometallated complexes of Pt$^{II}$. The associative substitution mechanism is still operative in this system. The orthometallated backbone has thus been manifested as a tool to make platinum(II) complexes react in a way very similar to that of palladium(II) complexes. We have already come across one such example.[40] The exchange of cyclopalladated ligands[41] involves monometallated palladium(II) dimeric complexes of the type $[\{Pd(C{-}N)X\}_2]$. Analogous platinum(II) complexes are not involved in the exchange because of their traditionally low lability. Bis complexes $[Pt(C{-}N)(C^*{-}N)]$, on the contrary, do participate and the role of the Pt–C bond of the first platinacycle is to increase the lability of the second one which undergoes the exchange. It may thus be possible to run reactions which occur for $Pd^{II}$, but are difficult to realize in the case of $Pt^{II}$, by using compounds with an orthoplatinated backbone.

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