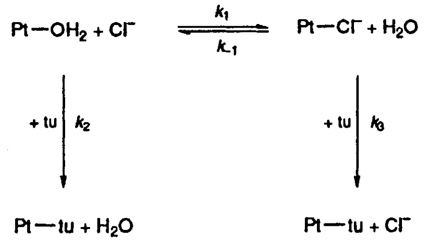
# Letter

## Tuning the reactivity of platinum(II) complexes through cyclometallation

In a recent paper[1] on the kinetics of the substitution reactions of the cyclometallated aqua complex $[Pt\{C_6H_4(CH_2NMe_2)\}(NC_5H_4SO_3\text{-}3)(H_2O)]$ **1** with various nucleophiles, the reactivity of the parent chloride complex was also studied by adding chloride to solutions of **1** prior to the addition of the reagent thiourea (tu). The mechanism proposed, Scheme 1, involves formation and solvolysis of the [PtCl] species (*via* $k_1$ and $k_{-1}$), and parallel bimolecular attack by thiourea on the aqua and chloride species (*via* $k_2$ and $k_3$). Data were interpreted by use of equation (1) derived using the steady-state approximation on (presumably) the aqua complex.



Scheme 1

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

A non-linear least-squares analysis gave $k_3 = 1950 \pm 150$ $dm^3\ mol^{-1}\ s^{-1}$ together with values of $k_1$, $k_{-1}$ and $k_2$ that were claimed to be consistent with those obtained from an independent study of the anation of **1** by chloride ($k_1 = 4000 \pm 75\ dm^3\ mol^{-1}\ s^{-1}$ and $k_{-1} = 34 \pm 2\ s^{-1}$) and thiourea ($k_2 = 55\,000 \pm 400\ dm^3\ mol^{-1}\ s^{-1}$).

However, a steady-state treatment can be applied only if and when (*i*) the concentration of the species in the steady state is very low, and (*ii*) the pathways competing for the steady state exhibit comparable rates. None of these conditions are fulfilled in the experiments described in ref. 1. Thus, from the distribution curves calculated using the reported equilibrium constant $K_{Cl} = 90 \pm 16\ dm^3\ mol^{-1}$, it is obvious that at least 30% of the starting material is in the form of the aqua complex for $[Cl^-] = 0.025\ mol\ dm^{-3}$. Under these conditions a large amount of the aqua complex has first to react, and almost disappear, before rate law (1) becomes valid. Examples of two parallel first-order reactions with widely different rates producing a common product are illustrated in textbooks,[2] but the present case is more complex, since the reversibility of the conversion of the aqua into the chloride species must also be taken into account. Scheme 1 can be expressed in general terms by equations (2)–(4), where A denotes $[Pt(H_2O)]$, B [PtCl] and

$$d[A]/dt = -k_1[A][Cl^-] - k_2[A][tu] + k_{-1}[B] \qquad (2)$$

$$d[B]/dt = -k_{-1}[B] - k_3[B][tu] + k_1[A][Cl^-] \qquad (3)$$

$$d[P]/dt = k_2[A][tu] + k_3[B][tu] \qquad (4)$$

P [Pt(tu)]. Fig. 1 shows the result of a numerical integration of these equations,[3] performed using the initial concentrations of $[Pt(H_2O)]$ and [PtCl] calculated from the equilibrium and rate constants given in ref. 1. It is obvious that the distribution ratio of the three species varies with time. Reactions are not strictly first-order until the concentration of the aqua complex becomes negligible, and the steady-state condition is fulfilled. As expected, the strongest initial deviations from pseudo-first-order behaviour are found for low concentrations of chloride and thiourea, but all kinetic runs follow biphasic and not monophasic behaviour, as claimed. Therefore, a simple first-order treatment based on equation (1) can be applied only to the final parts of the kinetic traces. The inconsistency of rate law (1) with Scheme 1 is also obvious from the fact that it predicts a rate expression $k_{obs} = k_{-1} + k_3[tu]$ in the absence of added chloride, which implies that the substitution is controlled by solvolysis (*via* $k_{-1}$) and nucleophilic attack (*via* $k_3$) on [PtCl], *i.e.* a species not present under these experimental conditions. The rate constants derived in ref. 1 should therefore be considered with some caution.

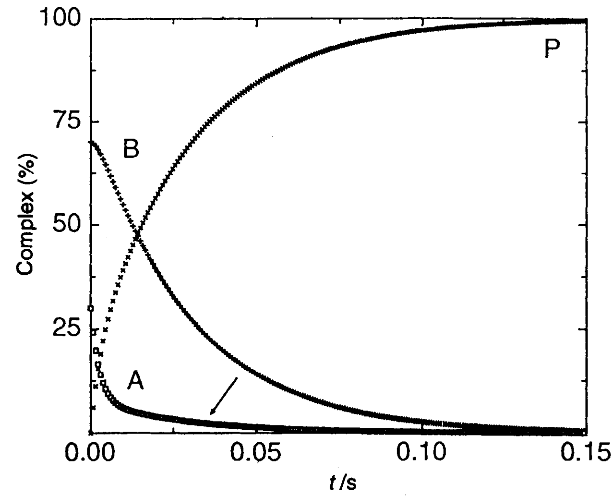


**Fig. 1** Calculated time dependence of the relative amounts of the starting complexes $[Pt(H_2O)]$ (A) and [PtCl] (B), and of the product [Pt(tu)] (P).[3] The arrow marks the time and the concentration of $[Pt(H_2O)]$ after which the value of the apparent rate constant remains constant and the steady-state approximation is valid. Experimental conditions: $[Pt(H_2O)] = 0.3 \times 10^{-4}\ mol\ dm^{-3}$, $[PtCl] = 0.7 \times 10^{-3}\ mol\ dm^{-3}$, $[Cl^-] = 0.025\ mol\ dm^{-3}$, $[tu] = 0.005\ mol\ dm^{-3}$

The interpretation of the other results in this paper[1] and in its preliminary communication[4] deserves some further comment. In the context of what has been known for more than three decades[5] about the chemistry of the platinum–carbon σ bond and its high ground state *trans* influence and high kinetic *trans* effect, there seems to be no value in singling out one such example, *viz.* that of a cyclometallate, as having an exceptional character of 'tuning and subtuning palladium reactivity towards platinum complexes'. This statement is based on comparisons of the reactivities of widely different, and as a matter of fact, not comparable systems, such as highly sterically hindered 'pseudo-octahedral' $[PdL(H_2O)]^{2+}$ (L = pentaalkyl-substituted derivatives of diethylenetriamine) complexes and the platinum(II) compound **1**, having a strongly *trans* labilizing Pt–C σ bond. In order not to be misleading, a comparison of reactivities must be based on the rates of analogous reactions of strictly similar compounds, in the present case for instance of the type [MX(N,R,N)] (M = Pt or Pd, R = alkyl or aryl, N = pyridine or amine, X = halide or $H_2O$). Noteworthy, the authors report that the rate of substitution of a palladium(II) complex having the same co-ordinative environment as **1** is too fast to be followed by their stopped-flow technique.[1]

Other examples from the literature show that the authors fall short of providing direct evidence for the metallacycle in the starting complex being the origin of the strong labilization of the aqua ligand *trans* to the platinum–carbon bond. Thus, the complex *trans*-$[Pt(PEt_3)_2Ph(MeOH)]^+$ reacts with chloride with a rate constant (1400 $dm^3\ mol^{-1}\ s^{-1}$)[6] comparable to that of **1** ($k_1$ = 4000 $dm^3\ mol^{-1}\ s^{-1}$), despite the encumbrance of its ligands and the perpendicular orientation of the aromatic ring relative to the co-ordination plane. Likewise, the strong σ-donor power of hydride causes the lability of the chloride ligand in *trans*-$[PtHCl(PEt_3)_2]$ in reactions with thiourea ($k_2$ = 6310 $dm^3\ mol^{-1}\ s^{-1}$)[7] to be comparable to that of the weakly co-ordinated water in **1** ($k_2$ = 55 000 $dm^3\ mol^{-1}\ s^{-1}$). Substitution of methanol for chloride in *trans*-$[Pt(PEt_3)_2Me(MeOH)]^+$ has a rate constant of $1.85 \times 10^4$ $dm^3\ mol^{-1}\ s^{-1}$ at 25 °C,[8] *i.e.* a value *ca.* four times larger than the value of $k_1$ reported as extraordinarily large for the metallacycle in ref. 1. It is also worth noting in this context that exchange processes in certain complexes of platinum- and palladium-(II) have been demonstrated to take place with similar rates for the two metal centres, depending on the nature of the ligands.[9]

To conclude, it is a well known fact that the co-ordination sites of platinum(II) complexes are labile under certain conditions, and that the reactivity can be 'tuned' or 'subtuned' by introducing suitable *trans* ligands.[5] Leaving aside the treatment in ref. 1 of the kinetics data related to the chloride complex, and the somewhat unconventional statement Pd ≡ Pt, it seems that the basic question raised by the authors in the title of their papers[1,4] 'to what extent can the Pt–C bond of a metallacycle labilize the *trans* position?' calls for the simple answer: as much as any other strongly *trans* labilizing platinum–carbon σ bond.

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**Schmülling *et al.* reply.** In an earlier paper we dealt with the question: to what extent can the platinum–carbon bond of a metallacycle labilize the *trans* position?[1] The emphasis in this paper was on the role of the platinum–carbon bond, and not on that of the metallacycle, although the latter aspect did form a part of our discussion. In the comment by Elding and Romeo, several aspects of the tuning of the reactivity of platinum(II) complexes *through cyclometallation* are discussed. They conclude that there seems to be no value in singling out one such example, *viz.* that of a cyclometallate, as having an exceptional character and offer an over-simplified answer to the question we raised.[1] Their comment offers us an opportunity to express our views once more, and to emphasize those aspects perhaps misconstrued by Elding and Romeo.

The main part of our paper[1] dealt with the substitution behaviour of two cyclometallated aqua complexes, *trans*-$[Pt\{C_6H_3X(CH_2NMe_2)\}(NC_5H_4SO_3\text{-}3)(H_2O)]$ '$[Pt(N\text{–}C,N)(H_2O)]$' (X = H or 3-MeO), and in a minor part we compared the reactivity of one aqua complex with that of the corresponding chloro complex. The addition of chloride enabled us to demonstrate that the chloro complex is *ca.* 30 times less labile than the corresponding aqua complex.[1] In the first part of their comment, Elding and Romeo reanalysed our data for the reaction in the presence of chloride and claim that the application of a steady-state treatment to the aqua complex is not appropriate under the selected experimental conditions. According to their analysis, 30% of the complex is in the aqua form at the *lowest* selected chloride concentration. This contribution of the aqua complex should result in biphasic kinetics and not in monophasic behaviour as we claimed.[1] Analysis of Fig. 1 clearly shows this expected biphasic behaviour under the limiting concentration conditions. At the higher concentrations of chloride selected in our study[1] this effect will be smaller since less of the complex is then in the aqua form. However, inspection of Fig. 1 demonstrates that the rapid initial disappearance of the aqua complex to less than 10% (see curve A in Fig. 1) occurs within the first 5 ms under these limiting conditions, followed by the subsequent monophasic decay for which the steady-state approximation should be valid. The first 5 ms are within the dead-time of most commercially available stopped-flow instruments, being typically between 2 and 4 ms (the employed Dionex D110 stopped-flow has a dead-time of 4 ms), and accounts for the fact that *no* biphasic kinetics were observed in any of our kinetic traces under the selected experimental conditions. From this we conclude that the observed monophasic behaviour is in agreement with the applied steady-state treatment.[1] Only a very few of the reported rate constants could really be affected by the outlined complication, such that the overall validity of our interpretation is not questionable.

Elding and Romeo also argue that our rate law (1) must be inconsistent with the suggested Scheme 1 since it reduces to $k_{obs} = k_{-1} + k_3[tu]$ in the absence of added chloride. This may sound like a convincing argument, but how can a rate law be valid under conditions where the mechanism is not valid anymore? In fact, both these comments have little to do with the tuning of the reactivity of platinum(II) complexes through cyclometallation, which is the theme of the comment.

In the second part of their comment, the authors focus on the interpretation of the results in our earlier papers.[1,4] They find a comparison between the investigated cyclometallated $[Pt(N\text{–}C,N)(H_2O)]$ complexes and a series of sterically hindered $[PdL(H_2O)]^{2+}$ (L = pentaalkyl-substituted derivatives of diethylenetriamine) complexes not appropriate and misleading. They prefer to compare the results for the cyclometallated complexes with those for complexes such as *trans*-$[Pt(PEt_3)_2Ph(MeOH)]^+$, *trans*-$[Pt(H)Cl(PEt_3)_2]$ and *trans*-$[Pt(PEt_3)_2Me(MeOH)]^+$, for which data have been published in the literature[6,7] or work that is unpublished. This leads to the conclusion 'that the authors fall short of providing direct evidence for the metallacycle in the starting complex being the origin of the strong labilization of the aqua ligand *trans* to the platinum–carbon bond'. As pointed out above, this was not the objective of our paper nor the question raised.[1] The systems cited by Elding and Romeo are all substitution reactions that occur in non-aqueous media and involve two *cis* labilizing phosphine ligands. They are therefore surely inappropriate for a comparison with the cyclometallated systems investigated in an aqueous medium.[1,4] It was clearly our objective to distinguish between steric and electronic effects in tuning the lability of $Pt^{II}$ and $Pd^{II}$ complexes in an aqueous medium. The N–N–N donor ligand arrangement in the series of complexes $[PdL(H_2O)]^{2+}$ was modified to a N–C,N arrangement in the systems investigated in order to study the effect of the introduction of a single Pt–C bond on the substitution behaviour of such square-planar complexes. The reported substitution rate constants are orders of magnitude higher than those of complexes containing only Pt–N bonds and demonstrate the *trans* labilization caused by the Pt–C bond. The details of the enhanced lability were further analysed in terms of back-bonding effects with the in-plane aryl ligand which increases the electrophilicity of the metal centre and assists the nucleophilic attack.[1] Furthermore, the in-plane arrangement diminishes steric hindrance which will support the associative attack. We never claimed the observed enhancement to be 'extraordinarily large', and are not surprised to find that substitution of methanol for chloride in *trans*-$[Pt(PEt_3)_2Me(MeOH)]^+$ (ref. 8) is *ca.* four times faster than found in our systems, especially when considering the effects of the solvent and the phosphine ligands mentioned above. In addition, we can also quote unpublished data which further strengthen our arguments and mechanistic assignment.[10]

The results of our investigation [1,4] have clearly demonstrated the extent to which a Pt–C bond can labilize the *trans* position in these cyclometallated N–C,N donor ligand complexes in aqueous solution. The in-plane aryl group obviously also plays an important role in controlling the electrophilicity of the central metal. In the present systems no evidence for a changeover in mechanism due to the enhanced labilization could be found; the substitution reactions all follow an associative mechanism. Notwithstanding the criticism raised by Elding and Romeo, we are convinced that the cited paper [1] is a worthy contribution to the understanding of the steric and electronic factors that control the lability of square-planar complexes. It summarizes basic principles, highlights various tuning abilities and demonstrates the beauty of structure–reactivity relationships. There has been a divergence of views regarding the possibility of a changeover in substitution mechanism from associative to dissociative being caused by increasing the steric hindrance in square-planar $Pt^{II}$ complexes.[11,12] We have explicitly demonstrated that steric hindrance itself can control the substitution rate but *not* the mechanism of square-planar substitution reactions. A combination of strong electronic labilization effects is required to cause a changeover in the substitution mechanism.[13,14] The detailed understanding of these effects remains in dispute.

To conclude, the question we raised 'to what extent can the Pt–C bond of a metallacycle labilize the *trans* position?' can be answered 'by four to five orders of magnitude, comparable to that reported for other *trans* labilizing Pt–C bonds, but not reported previously for organometallic platinum complexes in aqueous solution'.

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*Received* 27*th September* 1995; *Paper* 5/06407D

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