Steric and Electronic Tuning of the Lability of Square Planar d^8 Metal Complexes: Platinum(II) ≡ Palladium(II)

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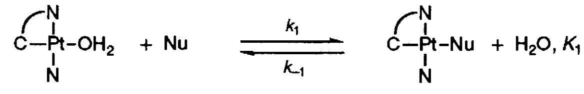
Electronic tuning of Pt^{II} complexes *via* cyclometallation, *i.e.* the introduction of a Pt–C bond *trans* to the leaving ligand, can increase their lability to that of related Pd^{II} complexes.

It is generally known that substitution reactions of square-planar complexes are approximately 10^6 times slower for Pt^{II} than for the corresponding Pd^{II} complexes, as in the case of solvent exchange on $M(H_2O)_4{}^{2+}$ and complex formation reactions of $M(dien)H_2O^{2+}$ (dien = diethylenetriamine, 1,4,7-triazaheptane), where M = Pt^{II} and Pd^{II}.[1–3] Earlier work in our laboratories showed that the introduction of steric hindrance can decrease the substitution rate of $Pd(R_5dien)H_2O^{2+}$ complexes by up to at least four orders of magnitude on going from R = H to R = Et,[4–6] such that the reactivity of Pd^{II} complexes can be slowed down systematically to reach the lability of related Pt^{II} complexes.

How can the lability of Pt^{II} complexes be increased to reach that of related Pd^{II} complexes? We have started work on a series of Pt^{II} complexes in which one N-donor is replaced by a C-donor atom, such that their reactivity can be compared with the series of dien complexes studied before. Thus, the influence of one metal–carbon bond, within the non-participating chelate ligand, on the substitution lability of the Pt^{II} centre can be studied systematically.

The way in which a Pt–C bond can be introduced, suggested by the recent work[7] on cyclopalladated monomeric complexes, is shown in Scheme 1. The $[Pt(\overset{\frown}{C\,N},N)(H_2O)]$ complex was prepared from the parent chloro-bridged dimer[8] by reaction with pyridine-3-sulfonic acid in pure water under heterogeneous conditions at 50 °C for *ca.* 3 days. The solvent water introduces a remarkable feature in the bridge-splitting process[9] in the way that the monomerization is accompanied by the hydrolysis of the labile chloro ligand to produce the aqua complex. This provides first evidence for the apparent strong *trans*-labilization effect of the Pt–C bond. In fact, it must be the *trans*-labilization since in the resulting complex the nitrogen donors are mutually *trans* and, correspondingly, the carbon donor must be *trans* to the coordinated water molecule. The evidence for the *trans*-configuration comes as usual from the upfield shift of the H6 proton of the *ortho*-platinated aryl ring owing to the anisotropic effect of coordinated pyridine.† The rapid hydrolysis may also partly arise from the negative charge on the pyridine ligand, since the negatively charged chloride ligand is no longer required to make the complex neutral. As a result the isolated complex is a zwitterion,[10] and it is slightly soluble in water to produce neutral solutions. This indicates that the sulfonic group must be deprotonated in the complex.

The *ortho*-platinated ligand in $[Pt(\overset{\frown}{C\,N},N)(H_2O)]$ lies in the metal plane, the metal–carbon bond is thus shorter than when the phenyl group is out of the plane.[7] Thus, a strong Pt–C interaction accompanied by a significant *trans*-labilization is expected. The substitution behaviour of this complex, reaction (1), was studied for a series of entering nucleophiles.



$$C\text{–}Pt(N)_2\text{–}OH_2 + Nu \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C\text{–}Pt(N)_2\text{–}Nu + H_2O,\ K_1 \qquad (1)$$

Nu = Cl^-, Br^-, I^-, thiourea

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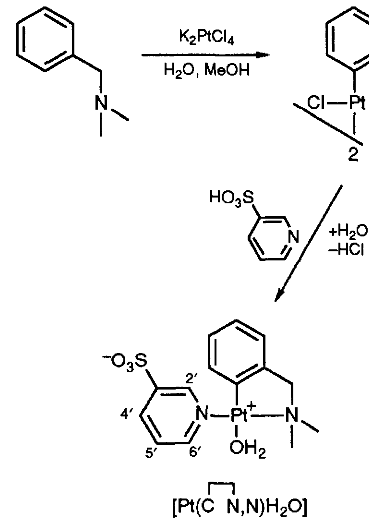
† [(2-Dimethylaminomethylphenyl-*C,N*)(3-pyridinesulfono-*N*)(aqua)-platinum(II)]. Satisfactory elemental analyses were obtained. ^1H NMR (400 MHz, δ, $[^2H_6]$DMSO): 3.32 (br s, Me), 4.07 (br s, CH_2), 5.85 (br, H6), 6.74 (t, H4), 6.97 (t, H5), 7.06 (br, H3), 7.69 (t, H5′), 8.29 (d, H4′), 8.94 (d, H6′), 9.1 (s, H2′). IR(KBr), ν/cm^{-1}: 1263 and 1170 ($-SO_3{}^-$).



Scheme 1

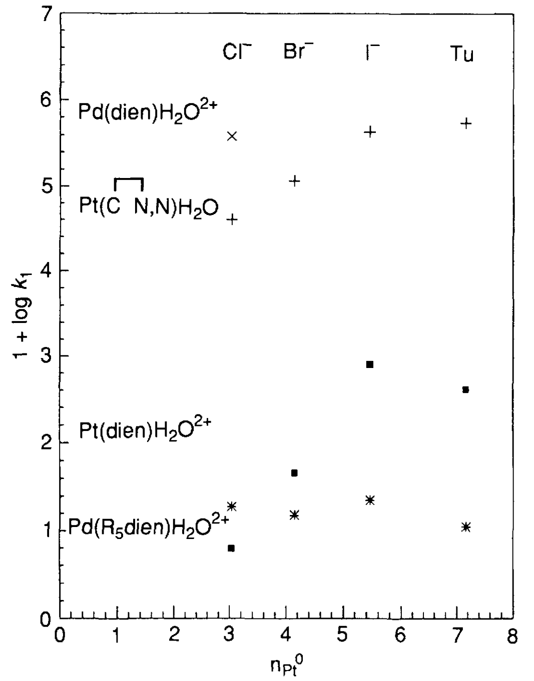


Fig. 1 A summary of kinetic data at 25 °C for a series of Pt^{II} and Pd^{II} complexes as a function of nucleophilicity of the entering ligand for the reaction $\mathrm{M(H_2O)} + \mathrm{Nu} \xrightarrow{k_1} \mathrm{M(Nu)} + \mathrm{H_2O}$; M = $\mathrm{Pd(dien)^{2+}}$ (×) (ref. 5), $\mathrm{Pt}(\overline{\mathrm{C\,N}},\mathrm{N})$ (+) (this work), $\mathrm{Pd(R_5dien)^{2+}}$ (*) (R_5 = 4-Me-1,1,7,7-Et_4 for Nu = Cl^-, Br^-, I^-; R_5 = 1,1,4,7,7-Et_5 for Nu = Tu) (ref. 4–6) and $\mathrm{Pt(dien)^{2+}}$ (■) (ref. 11).

Table 1 Observed and calculated rate constants for the system[a]

$$\mathrm{Pt}(\overline{\mathrm{CN}},\mathrm{N})\mathrm{H_2O} + \mathrm{Nu} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Pt}(\overline{\mathrm{CN}},\mathrm{N})\mathrm{Nu} + \mathrm{H_2O}$$

Nu	[Nu] × 10^3/ mol dm^{-3}	k_{obs}[b]/s^{-1}	k_1/dm^3 mol^{-1} s^{-1}	k_{-1}/s^{-1}
Cl^-	5	54 ± 3	4 000 ± 75	34 ± 2
	10	75 ± 6		
	25	132 ± 7		
	40	198 ± 7		
	50	232 ± 10		
Br^-	5	130 ± 3	11 290 ± 230	71 ± 7
	15	232 ± 7		
	25	364 ± 10		
	40	518 ± 23		
	50	637 ± 37		
I^-	0.5	78 ± 4	42 900 ± 520	59 ± 3
	1	102 ± 8		
	2.5	172 ± 11		
	4	233 ± 9		
	5	269 ± 11		
	10	489 ± 21		
Tu	0.5	26.8 ± 0.6	55 000 ± 380	−4 ± 2
	1	52 ± 1		
	2.5	127 ± 6		
	4	216 ± 5		
	5	271 ± 14		
	6	324 ± 13		
	8	439 ± 21		
	10	545 ± 29		

[a] Experimental conditions: $[Pt^{II}] = 5 \times 10^{-5}$ mol dm^{-3}; T = 25 °C; pH ≈ 4; ionic strength = 0.1 mol dm^{-3} ($NaClO_4$). [b] Mean value of at least six kinetic runs.

These reactions were studied under pseudo-first-order conditions using stopped-flow techniques,‡ and the observed kinetic data are summarized in Table 1. Plots of k_{obs} *vs.* nucleophile (Nu) concentration are linear with meaningful intercepts for chloride, bromide and iodide, which in terms of reaction (1) can be ascribed to the reverse aquation reactions, since $k_{obs} = k_{-1} + k_1$ [Nu]. This was confirmed by independent spectrophotometric equilibrium constant measurements, which resulted in K_1 = 90 ± 16, 141 ± 9 and 760 ± 20 dm^3 mol^{-1} for Nu = Cl^-, Br^- and I^-, respectively. These values are in close agreement with those calculated from the kinetic data in Table 1, *viz.* 117 ± 10, 159 ± 19 and 730 ± 50 dm^3 mol^{-1}, respectively. The absence of a noticeable intercept in the case of thiourea (Tu) as nucleophile is owing to the stronger binding of this particular 'soft' ligand to the metal centre such that k_{-1} is practically zero. The values of k_1 are compared to those found for the corresponding $\mathrm{Pt(dien)H_2O^{2+}}$, $\mathrm{Pd(dien)H_2O^{2+}}$ and $\mathrm{Pd(R_5dien)H_2O^{2+}}$ complexes in Fig. 1. The data demonstrate that the introduction of the metal–carbon bond increases k_1 by up to four orders of magnitude, such that the Pt^{II} orthometallated complex reaches a reactivity close to that of the sterically unhindered Pd^{II} complex. On the other hand, the reactivity of the $\mathrm{Pd(dien)H_2O^{2+}}$ complex can be reduced by four orders of magnitude by introducing five ethyl substituents, such that the complex reaches the reactivity of related Pt^{II} complexes.

The results of our investigation clearly demonstrate that the large difference in reactivity of corresponding Pt^{II} and Pd^{II} complexes (up to four orders of magnitude for the examples in Fig. 1), can be tuned by introducing either steric hindrance to slow down the Pd^{II} reactions, or introducing *trans*-labilization through cyclometallation to increase the reactivity of Pt^{II} complexes. This can be achieved with closely related systems and all in aqueous solution.

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‡ These reactions are characterized by an absorbance increase in the range 270 to 300 nm, which can be utilized for the kinetic measurements.

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