Substitution Reactions of Square Planar Complexes: Steric Crowding controls the Nucleophilicity Scale but not the Mechanism

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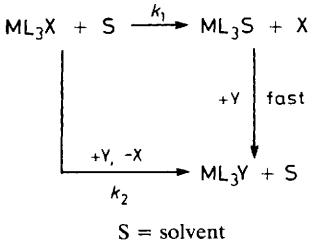
Rate and activation parameters for ligand substitution reactions on a severely sterically hindered Pd(II) complex indicate that steric crowding controls the nucleophilicity scale but not the nature of the substitution mechanism.

Substitution reactions of square planar d^8 metal complexes are in general accepted to proceed according to two parallel associative reaction paths.[1] One involves the rate-determining formation of a solvent ligand complex (k_1-path in Scheme 1) followed by rapid substitution of the co-ordinated solvent molecule (S). The other reaction involves direct nucleophilic attack by the entering ligand (k_2-path in Scheme 1). Under pseudo-first-order conditions (excess Y), the observed rate constant is a composite as indicated in equation (1). An

$$k_{obs} = k_1 + k_2[Y] \quad (1)$$

interesting aspect that has received significant attention from various kineticists[2–7] concerns the possibility of changing the substitution mechanism by increasing the steric crowding on the square planar complex, *i.e.* to prevent the associative attack of either a solvent molecule or another nucleophile. One such series of complexes that has been studied in detail concerns diethylenetriamine (dien) and substituted dien complexes of Pd^{II},[3–7] where introduction of methyl and ethyl groups on the N donor atoms produces 'pseudo-octahedral' complexes.[3] These investigations indicated that:[1] the solvolysis rate constant (k_1) can decrease by up to six orders of magnitude in going from the dien to the Et_5dien complex without any significant change in the values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$;[5,6] the usual nucleophilicity order $I^- > Br^- > N_3^- > Cl^-$ can change to $N_3^- > I^- > Br^- > Cl^-$ for the more sterically crowded complexes;[6] the k_2-path can disappear completely on increasing the steric crowding on the dien ligand.[3–5] These trends were recently also observed for solvent exchange and complex formation reactions of $Pd(R_5dien)H_2O^{2+}$ (R = H, Me, Et).[8] It follows that steric crowding on such square planar complexes can control the substitution behaviour (*i.e.* the nucleophilicity scale) but obviously, based on these data, not the fundamental nature of the substitution process.[5–8]

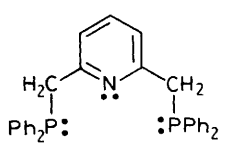


Scheme 1

It may be argued that the introduction of five ethyl substituents on the dien ligand is, by far, not enough to block the associative reaction path. For this reason we have turned our attention to a new series of complexes employing the ligand (**1**) (referred to as pnp) in which phenyl groups cause severe steric crowding.[9] A detailed study of a series of substitution reactions of the type shown in equation (2) revealed some remarkable findings reported here.

$$Pd(pnp)Cl^+ + L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Pd(pnp)L^{2+} + Cl^- \quad (2)$$

In the case of L = pyridine (py), both the chloro and pyridine complexes could be isolated as pure species,[9] which allowed us to study the kinetics of the reaction in equation (2) in both directions. Although Cl^- and py have very similar n_{Pt} values (3.04 and 3.19, respectively), their partial molar volumes differ significantly, *viz.*, 22.5 and 80.5 $cm^3\ mol^{-1}$, respectively. This must account for the significantly different kinetic data found at 25 °C in MeOH as solvent, *viz.* k_3 1.54 × 10^3 and k_{-3} 5.64 × $10^4\ mol^{-1}\ dm^3\ s^{-1}$. The overall equilibrium



(**1**)

constant for the reaction in equation (2), $K_3 = k_3/k_{-3} = 0.027$, reflects the difficulty encountered by the bulkier pyridine ligand in entering the co-ordination sphere of this complex. Thus a large excess of py is required to shift the equilibrium to the product side, whereas a 1 : 1 mixture of $Pd(pnp)py^{2+}$ and Cl^- almost quantitatively forms $Pd(pnp)Cl^+$.

The substitution reactions of $Pd(PNP)Cl^+$ were also studied for L = I^-, Me_4TU (TU = thiourea), and PPh_3; the corresponding values of k_3 (at 25 °C, MeOH as solvent) are 5.14×10^4, 4.63×10^3, and 1.31×10^3 mol^{-1} dm^3 s^{-1}, respectively. The observed reactivity order, $I^- > Me_4TU > PPh_3$, is exactly the reverse of the nucleophilicity order based on n_{Pt} values, *viz.* $PPh_3 > Me_4TU > I^-$, but correlates directly with the partial molar volume (*i.e.*, size) of the nucleophile, *viz.* 42.6 (I^-), 132 (Me_4TU), and 244 (PPh_3) cm^3 mol^{-1}.[9] It follows that steric hindrance on a square planar complex can inverse the nucleophilicity scale in the present system. Furthermore, the size of the entering nucleophile plays a dominant role in determining the rate of the substitution process. This suggests that steric and volume effects are more important than electronic effects in such nucleophilic substitution reactions.

The investigated reactions are all characterized by significantly negative $\Delta S^{\ddagger}$ (−100 to −150 J K^{-1} mol^{-1}) and $\Delta V^{\ddagger}$ (−7 to −13 cm^3 mol^{-1}) values,[9] which support the operation of an associative ligand substitution mechanism.[5,6,8] This is in good agreement with all of our previous findings on the dien system and demonstrates that steric hindrance merely slows down the associative attack of a bulky nucleophile, but does not prevent it. We conclude that steric crowding controls the nucleophilicity scale but not the nature of the mechanism in square planar substitution reactions.

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