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Catalyzed Substitutions on Cationic Palladium(II) Complexes. I. Kinetics of Acid-assisted Displacement of Coordinated Azido and Nitro Groups

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A kinetic study of the reactions of complexes of the type $[Pd(AAA)X]^+$ *(AAA = diethylenetriamine (dien); 1,1,7,7-tetraethyldiethylenetriamine (Et*$_4$*dien); 4-methyl-1,1,7,7,-tetraethyldiethylenetriamine (MeEt*$_4$ *dien); X =* NO_2 *and* N_3*) with* Cl^-*,* H^+ *and both* H^+ *and* Cl^- *in methanol at 25° C is reported.*

The rates of uncatalyzed displacement of nitro and azido groups by Cl^- *from axially blocked* $[Pd(Et_4dien)X]^+$ *depend on the chloride concentration, in contrast with the kinetic behaviour found for such substrates when X = Cl, Br and I, in which only the solvolytic path controls the substitution.*

The rate of proton assisted displacement follows the equation:

"rate" = $(k_1+k_2[Cl^-]+k_1'[H^+]+k_2'[H^+][Cl^-])$ *[Complex] which is consistent with a mechanism involving a nucleophilic attack by solvent and entering chloride on both the substrate and its protonated form in equilibrium. All rhe rate constants which appear in the rate equation have been determined and the values indicate that the acid controlled paths carry the major part of the reaction. The lability of the* NO_2 *group depends on the different orientation that it assumes with respect to the coordinate plane in unhindered or hindered complexes.*

Introduction

A great deal of work has been done[1] in octahedral systems on the way in which the proton affects the substitution of groups such as F^-, N_3^-, NO_2^-, CN^- *etc.* coordinated to a metal ion, particularly in the aquations of Co^{III}, Rh^{III} and Cr^{III} complexes. Comparatively few data can be found for 4-coordinate square planar complexes containing the same type of ligands. The observation that small amounts of perchloric acid accelerated the displacement of N_3^- and NO_2^- from some palladium(II) complexes containing the tridentate ligand diethylenetriamine or its N-alkyl substituted derivatives led us to study the kinetics of such systems in some detail.

This paper reports the rates of reaction of the complexes $[Pd(AAA)X]^+$ (AAA = diethylenetriamine (dien); 1,1,7,7-tetraethyldiethylenetriamine (Et$_4$dien) and 4-methyl-1,1,7,7-tetraethyldiethylenetriamine (MeEt$_4$dien); X = N_3 and NO_2) with Cl^-, H^+ and both H^+ and Cl^- in methanol at 30° C.

Experimental

Preparation of Complexes

[Pd(dien)X]NO_3 (X = N_3, NO_2) was obtained from [Pd(dien)Br]Br using literature methods.[2,3]

[Pd(Et$_4$dien)X]NO_3 (X = N_3, NO_2) was prepared by reacting [Pd(Et$_4$dien)Cl]Cl [3] with two equivalents of $AgNO_3$ in methanol. The AgCl was removed and the resulting methanol solution of [Pd(Et$_4$dien)NO_3]NO_3 was reacted with one equivalent of $NaNO_2$ or NaN_3. After evaporation of the solvent the resulting oil under vigorous stirring in a methanol–ether mixture gave the final products [Pd(Et$_4$dien)NO_2]NO_3 and [Pd(Et$_4$dien)N_3]NO_3 as white-yellow and deep yellow crystals respectively.

Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}N_3]NO_3$: C, 33.82; N, 23.01; H, 6.86. Found: C, 33.22; N, 22.87; H, 6.53. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}NO_2]NO_3$: C, 33.50; N, 16.28; H, 6.80. Found: C, 33.02; N, 15.84; H, 6.48.

[Pd(MeEt$_4$dien)X]PF_6(X = NO_2, N_3) was prepared by reacting [Pd(MeEt$_4$dien)Cl]PF_6[3] with one equivalent of $AgNO_3$ in methanol. The solution was stirred for 24 hr at room temperature, after which AgCl was removed and the solution reacted with one equivalent of NaX. After removal of most of the solvent, the mixture upon cooling gave the complexes [Pd(MeEt$_4$dien)N_3]PF_6 and [Pd(MeEt$_4$dien)NO_2]PF_6 which were isolated by filtration and re-crystallized from methanol as orange-yellow and pale-yellow products, respectively.

Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_3)(CH_2)_2N(C_2H_5)_2\}N_3]PF_6$: C, 29.80; N, 16.04; H, 5.98. Found: C, 29.90; N, 15.93; H, 5.87. Calcd.

for $[Pd\{(C_2H_5)_2N(CH_2)_2N(CH_3)(CH_2)_2N(C_2H_5)_2\}NO_2]PF_6$: C, 29.58; N, 10.61; H, 5.92. Found: C, 29.71; N, 10.83; H, 5.68.

All the compounds were characterized through their u.v. and i.r. spectra. The molar conductivities in methanol at 18° C are in the range 80–90 ohm^{-1} cm^2 mol^{-1} and are consistent with those of 1 : 1 electrolytes[4].

Isolation and Characterization of $[Pd(dien)H_2O](ClO_4)_2$

Methanol solutions of $[Pd(dien)N_3]NO_3$ or $[Pd(dien)NO_2]NO_3$ were mixed with aqueous perchloric acid in the ratio 1:20. After removal of the solvent, the resulting oil under vigorous stirring in ether changed slowly into a fine product which was recrystallized from a methanol–ether mixture. Calcd. for $[Pd\{NH_2(CH_2)_2NH(CH_2)_2NH_2\}H_2O](ClO_4)_2$: C, 11.26; N, 9.84; H, 3.54; Cl, 16.61. Found: C, 11.56; N, 10.05; H, 3.40; Cl. 17.23.

The formulation suggested for this aquo-complex is consistent with (i) the analytical data, (ii) the i.r. spectrum which indicates the presence of coordinated water (νO–H = 3550 cm^{-1}), (iii) the molar conductivity of 230 ohm^{-1} cm^2 mol^{-1} in acetone at a complex concentration of $10^{-4}M$, typical of 1:2 electrolytes[4]. Hartley has recently reported the preparation of this aquo-complex[5] and of its platinum(II) analogue[6] by other routes.

The u.v. spectrum obtained at the end of the reaction of $[Pd(dien)N_3]NO_3$ and $[Pd(dien)NO_2]NO_3$ with $HClO_4$ in methanol is identical to that of $[Pd(dien)H_2O](ClO_4)_2$ under the same conditions of acidity. All attempts to isolate aquo-derivatives of substrates containing N-alkyl substituted diethylenetriamine were unsuccessful. Nevertheless their existence was proved in solutions and in the case of $[Pd(Et_4dien)H_2O](ClO_4)_2$ the spectral characteristics in the u.v. region are identical to that previously reported by Basolo *et al.*[7]

In the reactions with H^+ and Cl^- the final product obtained by the mentioned procedure always was the chloro–chloride.

Methanol was purified by distillation after refluxing over $Mg(OCH_3)_2$. $HClO_4$, LiCl and $LiClO_4$ were all reagent grade.

Spectra

Ultraviolet spectra were recorded on an Optica CF 4R spectrophotometer in 1 cm quartz cells. Infrared spectra were recorded with a Perkin–Elmer Mod. 457 instrument by mulling the sample in nujol.

Kinetics

Slow reactions were followed by standard spectrophotometric techniques using an Optica CF 4R instrument. Known volumes of methanol solutions of the substrate and reagent were brought separately to 25° C and mixed in the thermostated cell of the spectrophotometer. The reactions were followed by measuring the changing optical density of the reaction mixture in the u.v. region at selected wavelengths where the difference between the absorption of the starting complex and that of the final product was largest.

Fast reactions were followed by the "stopped-flow" method using a Durrum–Gibson instrument equipped with thermostated glass drive syringes and a teflon mixing chamber. The temperature was controlled to within ± 0.1° C. Transmittance changes at a selected wavelength during the course of reaction were displayed on a storage oscilloscope and traces were photographed with a Polaroid camera. Values obtained from duplicate experiments were in good agreement.

A large excess of reagent was always used to provide pseudo-first-order conditions and to force the reactions to completion. Pseudo-first-order rate constants k_{obsd} (s^{-1}) were calculated from the gradients of the plots of $\log(D_t-D_\infty)$ against time (D_t is the optical density at time t and D_∞ that at the end of reaction). In all the kinetic runs the ionic strength was kept constant at 0.1 *M* by adding the required amount of $LiClO_4$ to the reaction mixture.

Results

Uncatalyzed Nucleophilic Substitutions

The pseudo-first-order rate constants in Table I for the reactions:

$$[Pd(AAA)X]^+ + Cl^- \rightarrow [Pd(AAA)Cl]^+ + X^- \qquad (1)$$

were determined at various chloride concentrations within the range 0.005–0.1 *M*. In the case of complexes containing Et_4dien as ligand these constants, k_{obsd}, when plotted against Cl^- gave straight lines with non-zero intercepts indicating that the usual two-term rate equation, $k_{obsd} = k_1 + k_2[Cl^-]$, is obeyed. For complexes with $MeEt_4$dien the entry of the nucleophile occurs with a rate independent of its concentration and the k_2 term disappears.

Acid Assisted Solvolysis

The rate of the reactions:

$$[Pd(AAA)X]^+ + H^+ + MeOH \rightarrow [Pd(AAA)MeOH]^{++} + HX \qquad (2)$$

were followed by varying the concentration of $HClO_4$ within the range 0.01–0.1 *M* (Table II).

Plots of k_{obsd} against $[H^+]$ were linear according to a rate law of the type: $k_{obsd} = k_1 + k_1'[H^+]$. The acid-independent term k_1 was identical to that obtained in the uncatalyzed substitutions, but its contribution to the reaction was small except at the lowest proton concentrations.

TABLE I. Pseudo-first-order Rate Constants, k_{obsd}, for the Reactions $[Pd(AAA)X]^+ + Cl^- \rightarrow [Pd(AAA)Cl]^+ + X^-$ in Methanol at 25° C, $\mu = 0.1 M$.

Complex	$[Cl^-]$, *M*	$10^6 k_{obsd}(s^{-1})$	Complex	$[Cl^-]$, *M*	$10^6 k_{obsd}(s^{-1})$
$[Pd(Et_4dien)N_3]^+$	0.008	1.3	$[Pd(MeEt_4dien)N_3]^+$	0.036	1.0
	0.016	2.0		0.056	1.0
	0.036	3.5		0.08	1.0
	0.056	4.5		0.10	1.0
	0.08	6.5			
	0.10	7.8			
			$[Pd(MeEt_4dien)NO_2]^+$	0.036	6.5
				0.056	6.5
$[Pd(Et_4dien)NO_2]^+$	0.036	13.6		0.08	6.6
	0.056	15.5		0.10	6.9
	0.08	17.3			
	0.10	19.5			

TABLE II. Pseudo-first-order Rate Constants, k_{obsd}, for the Reactions $[Pd(AAA)X]^+ + H^+ + MeOH \rightarrow [Pd(AAA)MeOH]^{++} + HX$ in Methanol at 25° C, $\mu = 0.1 M$.

Complex	$10^2[H^+]$, *M*	$k_{obsd}(s^{-1})$	Complex	$10^2[H^+]$, *M*	$k_{obsd}(s^{-1})$
$[Pd(dien)NO_2]^+$	2.0	0.90×10^{-2}	$[Pd(Et_4dien)N_3]^+$	2.0	2.98×10^{-4}
	4.0	1.65×10^{-2}		4.0	5.40×10^{-4}
	6.0	2.24×10^{-2}		6.0	8.30×10^{-4}
	8.0	3.02×10^{-2}		8.0	11.5×10^{-4}
				10.0	14.3×10^{-4}
$[Pd(dien)N_3]^+$	0.4	4.2	$[Pd(MeEt_4dien)NO_2]^+$	2.0	1.45×10^{-5}
	2.0	21.9		4.0	1.86×10^{-5}
	4.0	52.9		6.0	2.50×10^{-5}
	6.0	74.1		8.0	2.70×10^{-5}
	8.0	96.0		10.0	2.91×10^{-5}
$[Pd(Et_4dien)NO_2]^+$	2.0	2.85×10^{-5}	$[Pd(MeEt_4dien)N_3]^+$	2.0	3.20×10^{-5}
	6.0	4.80×10^{-5}		4.0	6.90×10^{-5}
	10.0	6.60×10^{-5}		6.0	9.85×10^{-5}
				8.0	13.8×10^{-5}
				10.0	17.7×10^{-5}

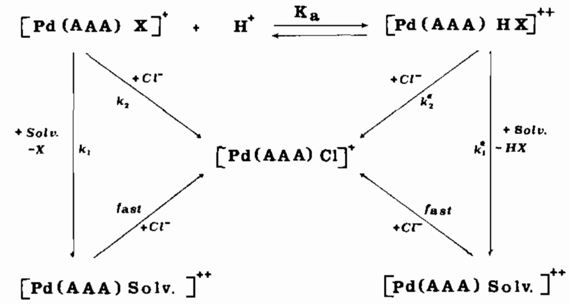
Acid-assisted Nucleophilic Substitutions

The kinetics of the reaction:

$$[Pd(AAA)X]^+ + H^+ + Cl^- \rightarrow [Pd(AAA)Cl]^+ + HX \quad (3)$$

were followed at various proton and chloride concentrations and the values of the pseudo-first-order rate constants k_{obsd} (s^{-1}) are collected in Table III. At constant concentration of acid, the plots of k_{obsd} *vs.* $[Cl^-]$ are linear and slopes and intercepts are all acid dependent. Likewise, at a constant concentration of chloride, plots of k_{obsd} against $[H^+]$ are linear and the slopes and intercepts are chloride dependent.

All the kinetic observations can be accounted for by the following reaction scheme:



which involves a rapid pre-equilibrium between the substrate and its mono-protonated reactive species.

TABLE III. Pseudo-first-order Rate Constants k_{obsd}, for the Reactions $[Pd(AAA)X]^+ + H^+ + Cl^- \rightarrow [Pd(AAA)Cl]^+ + HX$ in Methanol, at 25° C, $\mu = 0.1\,M$.

Complex	$10^3[H^+]$, *M*	$10[Cl^-]$, *M*	$10^3k_{obsd}(s^{-1})$	Complex	$10^3[H^+]$, *M*	$10[Cl^-]$, *M*	$10^3k_{obs}(s^{-1})$
$[Pd(dien)NO_2]^+$	2.00	0.08	3.30	$[Pd(dien)N_3]^+$	0.50	0.16	1,300
	2.00	0.16	4.40		0.50	0.36	3,220
	2.00	0.36	6.70		0.50	0.56	5,460
	2.00	0.56	9.20		0.50	0.76	7,000
	4.00	0.08	4.60		1.00	0.16	3,350
	4.00	0.16	6.20		1.00	0.36	9,250
	4.00	0.36	10.00		1.00	0.56	15,500
	4.00	0.56	13.70		1.00	0.76	21,000
	6.00	0.08	6.00		2.00	0.16	11,500
	6.00	0.16	8.00		2.00	0.36	25,000
	6.00	0.36	13.20		2.00	0.56	38,000
	6.00	0.56	18.40		2.00	0.76	52,000
	8.00	0.08	7.30		4.00	0.16	21,000
	8.00	0.16	10.00		4.00	0.36	47,000
	8.00	0.36	16.20		4.00	0.56	80,600
	8.00	0.56	22.40		4.00	0.76	104,000
$[Pd(Et_4dien)N_3]^+$	0.50	0.08	0.08	$[Pd(MeEt_4dien)NO_2]^+$	0.50	0.08	0.02
	0.50	0.16	0.27		0.50	0.16	0.04
	0.50	0.36	1.20		0.50	0.36	0.09
	0.50	0.56	2.10		0.50	0.56	0.14
	0.50	0.76	3.30		0.50	0.76	0.20
	0.50	0.96	4.10				
					1.00	0.08	0.045
	1.00	0.08	0.39		1.00	0.16	0.077
	1.00	0.16	1.20		1.00	0.36	0.14
	1.00	0.36	3.70		1.00	0.56	0.22
	1.00	0.56	5.20				
	1.00	0.76	7.07		2.00	0.16	0.13
	1.00	0.96	9.70		2.00	0.36	0.32
					2.00	0.56	0.44
	2.00	0.08	1.50		2.00	0.76	0.64
	2.00	0.16	2.66				
	2.00	0.36	7.00	$[Pd(MeEt_4dien)N_3]^+$	0.50	0.08	0.088
	2.00	0.56	11.00		0.50	0.16	0.17
	2.00	0.76	15.00		0.50	0.36	0.45
	2.00	0.96	19.20		0.50	0.56	0.73
					0.50	0.76	0.95
	3.00	0.08	2.00				
	3.00	0.16	4.00		1.00	0.08	0.26
	3.00	0.36	10.00		1.00	0.16	0.50
	3.00	0.56	15.00		1.00	0.36	1.18
					1.00	0.56	1.79
$[Pd(Et_4dien)NO_2]^+$	1.00	0.56	0.42				
	2.00	0.56	0.85				
	3.00	0.56	1.33				
	4.00	0.56	1.77				

k_1 and k_1* are the rate constants of the reaction paths in which the solvent attacks the substrate and the protonated species respectively, forming a labile solvento intermediate $[Pd(AAA)MeOH]^{++}$ which undergoes fast anation by Cl^- yielding the product $[Pd(AAA)Cl]^+$. k_2 and k_2* are the rate constants for the bimolecular attack by chloride on the same two species in equilibrium. K_a is the constant related to the equilibrium:

$$K_a = \frac{[Pd(AAA)XH]^{2+}}{[Pd(AAA)X]^+[H^+]}$$

Under pseudo-first-order conditions, where $[H^+]$ and $[Cl^-]$ remain constant in any run, a treatment of the

TABLE IV. Specific Rate Constants for Uncatalysed and Catalysed Displacement of X from $[Pd(AAA)X]^+$ in Methanol at 25° C, $\mu = 0.1 M$.

Complex	Uncatalysed		Catalysed	
	$k_1(s^{-1})$	$k_2(M^{-1} s^{-1})$	$k_1'(M^{-1} s^{-1})$	$k_2'(M^{-2} s^{-1})$
$[Pd(dien)NO_2]^+$	1.2×10^{-3} [a]	6.2×10^{-2} [a]	3.6×10^{-1}	33
$[Pd(dien)N_3]^+$	3.0×10^{-2} [a]	1.0[a]	1.2×10^{3}	3.5×10^{5}
$[Pd(Et_4dien)NO_2]^+$	1.0×10^{-5}	9.3×10^{-5}	4.7×10^{-4}	8
$[Pd(Et_4dien)N_3]^+$	1.0×10^{-6}	6.8×10^{-5}	1.4×10^{-2}	95
$[Pd(MeEt_4dien)NO_2]^+$	6.0×10^{-6}	–	1.9×10^{-4}	4.3
$[Pd(MeEt_4dien)N_3]^+$	1.0×10^{-6}	–	1.7×10^{-3}	24

[a] Data from reference 29.

reactions in the scheme (it being assumed that the concentration of $[Pd(AAA)MeOH]^{2+}$ remains small and negligible), leads to the relationship:

$$k_{obsd} = \frac{k_1 + k_2[Cl^-] + k_1^*K_a[H^+] + k_2^*K_a[H^+][Cl^-]}{1 + K_a[H^+]} \quad (4)$$

Since no departure from a first-order dependence on $[H^+]$ was observed in the plots of k_{obsd} *vs.* $[H^+]$ at constant chloride concentration, it can be assumed that the equilibrium is well over to the unprotonated substrate. If $K_a[H^+] \ll 1$ equation (4) assumes the form:

$$k_{obsd} = k_1 + k_2[Cl^-] + k_1'[H^+] + k_2'[H^+][Cl^-] \quad (5)$$

where k_1' and k_2' are composite terms given by the products $k_1^* \cdot K_a$ and $k_2^* \cdot K_a$, respectively. The values of all the rate constants that appear in eq. (5) were determined and are collected in Table IV.

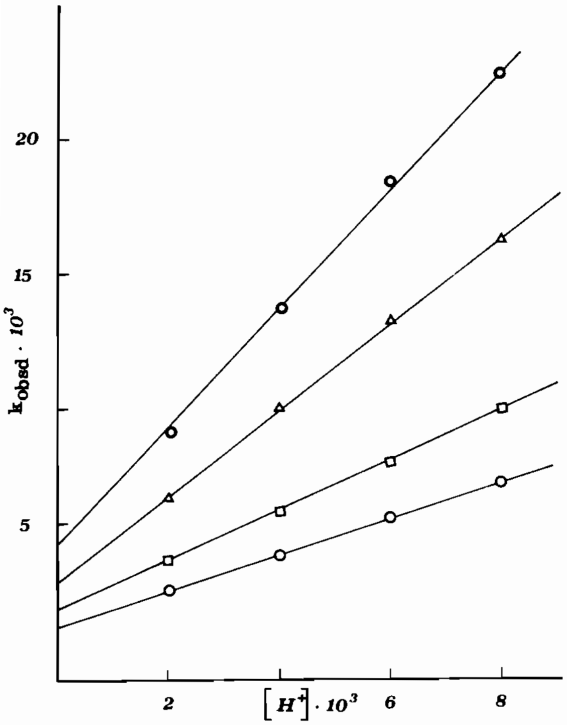


Figure 1. Dependence of pseudo-first-order rate constants (k_{obsd}) on $[H^+]$ for the reactions $[Pd(dien)NO_2]^+ + H^+ + Cl^- \rightarrow [Pd(dien)Cl]^+ + HNO_2$ in methanol at 25° C, $\mu = 0.1 M$. Complex $= 2.5 \times 10^{-4} M$; ○$[Cl^-] = 0.008 M$; □$[Cl^-] = 0.016 M$; ▲$[Cl^-] = 0.036 M$; ●$[Cl^-] = 0.056 M$.

The rate constants k_1 and k_2 were accurately determined from the straight lines obtained on plotting k_{obsd} against $[Cl^-]$ in the uncatalyzed substitutions, where eq. (5) assumes the form $k_{obsd} = k_1 + k_2[Cl^-]$. Likewise the k_1' values were obtained as slopes of linear plots of k_{obsd} *vs.* $[H^+]$ in the kinetics of catalyzed solvolysis where eq. (5) is reduced to the simpler form $k_{obsd} = k_1 + k_1'[H^+]$. The pseudo-first-order rate constants (k_{obsd}) obtained in the acid-assisted nucleophilic substitutions, when plotted against $[H^+]$ at constant chloride concentrations, give a sheaf of straight lines (Figure 1), the intercepts and slopes of which are chloride dependent, being equal to $k_1 + k_2 [Cl^-]$ and $k_1' + k_2'[Cl^-]$, respectively. On plotting the values of these intercepts and slopes against the chloride concentration it is possible to obtain all the rate constants and to check the consistency of k_1', k_1 and k_2 with the values previously determined.

Discussion

Uncatalyzed Nucleophilic Substitutions

In order to see the effect of steric hindrance in an associative process Basolo[3,7] studied the rates of reactions of halide ions with $[Pd(Et_4dien)X]^+$ (X = Cl, Br, I) in aqueous solution. It was found that in these axially blocked Pd^{II} complexes the reagent dependent path (k_2) is depressed and the rate of halide displacement is independent of the nature and concentration of reagents. The pathway of the substitution involves a slow solvolysis step, followed by fast anation of the reactive aquo-intermediate. Later on Gray *et al.*[8] found that the same pattern of behaviour holds in a series of protic and dipolar aprotic solvents. Discussing the mechanistic role of the solvent in the solvolytic path, their conclusion was that the Et_4dien ligand imposes so severe steric restrictions to the approach of a nucleophile to the central metal ion that only small molecules qualify. Therefore reactions in protic solvents involve associative activation, whereas in aprotic solvents such as DMSO, which is unable to interact effectively with Pd^{II}, a dissociative mechanism is probable. In this case solvation of the leaving group provides stabilization for the transition state.

In sharp contrast with these findings, our results show that using Cl^- as entering nucleophile the kinetics of the complexes $[Pd(Et_4dien)X]^+$ ($X = N_3$, NO_2) in methanol exhibit a definite k_2 term, while k_1 is greatly reduced with respect to that of the halide ions, giving the following sequence of lability $Cl \simeq Br \simeq I > NO_2 > N_3$. The rate dependence on the concentration of Cl^- indicates that a direct bimolecular attack by reagents other than the solvent is possible and it is displayed when solvation of the leaving anion is less effective in helping Pd–X bond breaking. In a number of cases in which a k_2 term has been observed in the kinetics of these sterically hindered complexes, some particular mechanism was invoked. In fact the rate dependence on the concentration of OH^- has been attributed to an S_N1cb mechanism[3] and that of the thiosulfate ion to its very large nucleophilicity[7]. Furthermore the k_2 term that appears with bulky outgoing groups such as selenocyanide[9] when acetonitrile[10] is used as solvent, was attributed to the enhanced possibility of a spread of ethyl groups allowing the entrance of the incoming nucleophile. It is known that steric hindrance created by the Et_4dien ligand causes linkage isomerization with ambidentate thiocyanate and selenocyanate which in solution are forced to switch from the more favorable Pd–SCN and Pd–SeCN "soft–soft" interactions to Pd–NCS and Pd–NCSe linkages[11, 12, 13]. A similar influence would be expected on the bonding mode of ambidentate NO_2, favouring a nitro–nitrito linkage isomerization. Analysis of the i.r. spectrum of $[Pd(Et_4dien)NO_2]NO_3$ showed clearly that the solid complex was an N-bonded stable species and it maintains its identity in solution.

In order to obtain further insight into the bonding mode of nitro-derivatives an X-ray diffraction study has been carried out on $[Pd(dien)NO_2]NO_3$ and $[Pd(Et_4dien)NO_2]NO_3$[14]. The molecular structure shows that the main difference in the two complexes deals with the orientation of NO_2 groups with respect to the coordination plane, being coplanar in $[Pd(dien)NO_2]NO_3$ and normal in $[Pd(Et_4dien)NO_2]NO_3$ while $Pd–NO_2$ bond lengths do not vary significantly. The coplanar orientation is presumably due, as in the case of $[Pd(NH_3)_3NO_2]_2$ and $[Pd(NH_3)_4](NO_3)_4$ [15] to intermolecular hydrogen bonds $NH_2 \cdots O_2N–$ whereas the presence of ethyl substitutents does not allow the possibility of hydrogen bonds and it forces the NO_2 plane to assume a normal orientation. On the contrary the bonding mode of N_3 does not vary significantly on going from $[Pd(dien)N_3]NO_3$ to $[Pd(Et_4dien)N_3]NO_3$[16].

Although some caution must be taken in correlating structural and reactivity data these kinetics strongly support the hypothesis of an "anchoring" effect on the nitro group by hydrogen bonds in the unhindered system. In fact, the ratio of the solvolysis rates for $[Pd(dien)X]^+$ complexes $k_1(Pd–N_3)$ / $k_1(Pd–NO_2)$ is 25 whereas it is reduced to 0.1 and 0.15 on going to $[Pd(Et_4dien)X]^+$ and $[Pd(MeEt_4dien)X]^+$, respectively.

In other words N_3 is a better leaving group than NO_2 in unhindered complexes and the presence of ethyl groups causes an inversion in lability. Although less evident, the inversion of lability is found also in the reagent dependent path (k_2).

Acid-assisted Nucleophilic Substitutions

In the reaction scheme there appears a rapid pre-equilibrium between the substrate and a monoprotonated labile species which is presumably formed by the proton attack on the basic groups N_3 and NO_2 coordinated to the metal. This attack causes a weakening of Pd–N bond and favours an ease removal of the group. Such an attack is very common in octahedral systems and in this context it is interesting to note that Co^{III} complexes containing HNO_2 and HN_3 as coordinated groups have been isolated[17, 18].

Likely alternative mechanisms could involve (i) an opening of the chelate ring with an equilibrium between the chelate complex and a reactive "open ring" species having a quaternary terminal nitrogen[19] or (ii) an electrophilic attack by H^+ on the metal, forming labile intermediates at higher oxidation state, as found on the complexes $[Pt(PEt_3)_2(C_6H_5)_2]$[20] and $[Pt(PEt_3)_2(CH_3)X]$[21] containing platinum–carbon bonds, in the deuterium–hydrogen exchange on $[Pt(PEt_3)_2(H)Cl]$[22] and in the reaction of *trans*-$[Pt(pyperidine)_2Cl_2]$ with nitrous acid[23].

However, the fact that no evidence for acid catalysis has been found in the reactions of the corresponding halide complexes of the type $[Pd(Et_4dien)X]^+$ ($X =$ Cl, Br, I) is a clear indication in favour of the pre-equilibrium shown in the reaction scheme. Furthermore halide complexes undergo metal catalysis by Hg^{++} and Cd^{++} through an attack of these cations on the Pd–X bond[24].

By comparing the catalytic rate constants of complexes containing the same N-alkyl substituted amine as ligand (Table IV) it can be seen that azido complexes are much more sensitive to the effect of H^+ than nitro derivative. Since the catalytic constants are composite terms it is not possible to establish whether the effectiveness of H^+ is due only to its greater affinity towards the coordinated N_3 with respect to NO_2 determining a wider extension of the acid pre-equilibrium or also to a somewhat different reactivity of the two protonated groups.

On going to $[Pd(dien)X]^+$ the value of the catalytic constant of the azido compound is dramatically enhanced, as a result of a decrease in steric hindrance, whereas that of the nitro derivative remains substantially unchanged. Once again this result is in agreement with the hypothesis of a different $Pd–NO_2$ bonding mode in unhindered and hindered systems. In the complex containing diethylenetriamine as ligand the hydrogen bonds $-NO_2-_2HN-$ not only make the removal of NO_2 less easy but also make its oxygens less available to electrophilic attack by H^+, thereby reducing the value of K_a. Steric factors which favour the bimolecular nucleophilic attack are largely compensated by a minor extension of the acid equilibrium coupled with a lower lability of the protonated NO_2 group, so that the catalytic effect of H^+ on all nitro compounds results almost the same, regardless of the nature of the ancillary ligands.

The fact that the rates of catalysed displacement on nitro compounds depend on chloride concentration leads us to exclude the possibility of an intermolecular rearrangement of $[Pd(chelate)NO_2H]^{++}$ in the rate determining step, as found in the acid catalysed hydrolysis of $[Co(NH_3)_5NO_2]^{2+}$[25] and of *cis* and *trans*-$[PtA_2(NO_2)_2]$[26,27] (A = neutral molecule). Likewise the intermediacy of reactive nitrene compounds in the reactions of azido complexes with acid, as found by Basolo[28] on $[Ir(NH_3)_5N_3]^{2+}$, is to be excluded in our case on the basis of the nature of the product obtained and the absence of nitrogen evolution.

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