Fast Reactions at Planar Four-co-ordinate Complexes. Part I. Nucleophilicity Towards Palladium(II) Complexes

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Rates of nucleophilic substitution reactions (i) [L = PPr^n_3, $AsEt_3$, or piperidine, $C_5H_{11}N$; $Y^- = Cl^-, N_3^-, Br^-, I^-, SCN^-$, or $(NH_2)_2CS$] have been measured in methanol at 25 °C. A set of nucleophilic reactivity constants,

$$trans\text{-}[PdL_2(NO_2)_2] + Y^- \longrightarrow trans\text{-}[PdL_2(NO_2)Y] + NO_2^- \qquad \text{(i)}$$

$n_{Pd}^0 = \log (k_2[MeOH]/k_1)$, have been calculated, k_1 and k_2 referring to rate constants for the solvolytic path and for direct nucleophilic attack on the complex *trans*-$[Pd(PPr^n_3)_2(NO_2)_2]$. All the complexes studied obey the linear free-energy relation $\log k_2 = sn_{Pd}^0 + \log k_1$, where s is a nucleophilic discrimination factor. The n_{Pd}^0 sequence resembles that already found for platinum(II) complexes.

MOST information regarding rates of nucleophilic substitution reactions of d^8 square-planar substrates comes from studies of platinum(II) complexes [1] and to a lesser extent from those of gold(III) and palladium(II) [2] which are much more labile. The use of new experimental techniques for the study of fast reactions has allowed systematic studies of the reactivity of palladium(II) complexes.[3] The best way of rationalizing kinetic data for a series of reactions is to seek a linear free-energy relation,[4] that is to correlate the reactivity of reagents with some of their extra-kinetic properties.

As far as co-ordination compounds are concerned, nucleophilic reactivity has been discussed in terms of reagent basicity toward the proton or some other property such as polarizability, redox potential, or electronegativity.[5-7] These last factors are a measure of electronic deformation and of the ease with which electrons are transferred from the nucleophile to the metal. For planar platinum(II) complexes, no correlation has been found between nucleophilic reactivity and any one extra-kinetic factor and the most efficient reactivity sequence is that expressed by the n_{Pt} scale.[8-10] It has been also pointed out that these complexes follow equation (1), where s is a nucleophilic discrimination

$$\log k_2 = \log k_1 + sn_{Pt}^0 \qquad (1)$$

factor, and k_1 and k_2 refer to the reaction of the complex with the solvent and nucleophile respectively. Little is known of the possibility of applying such relations to associative substitution reactions of palladium(II) complexes. This paper reports a detailed investigation of reactions (2) (L = PPr^n_3, $AsEt_3$, or piperidine; Y = Cl^-, N_3^-, Br^-, I^-, SCN^-, or $(NH_2)_2CS$ in methanol at 25 °C).

$$trans\text{-}[PdL_2X_2] + Y \longrightarrow trans\text{-}[PdLXY] + X \qquad (2)$$

EXPERIMENTAL

All the complexes studied were obtained by published methods [11-12] and characterized through i.r. spectra and elemental analysis. Methanol was purified by distillation after heating under reflux over $Mg(OMe)_2$. All other products were reagent grade.

Kinetics.—Slower reactions were followed by standard spectrophotometric techniques in the visible and u.v. region using an Optica CF4R instrument. Spectral changes during the reactions were recorded and in many cases the spectra showed well defined isosbestic points indicating the presence of only two absorbing species, *i.e.* the starting substrate and the final product. All reactions were followed in the presence of a large excess of reagent in order to provide pseudo-first-order conditions and to force the reactions to completion. Judging from results obtained with various nucleophiles at different concentrations of $LiClO_4$, the effect of ionic strength is small, as expected for processes involving neutral substrates. Pseudo-first-order rate constants k_{obs} (s^{-1}) were determined from gradients of plots of $\log (A_\infty - A_t)$ against time (A_t is the optical density at time t and A_∞ that at the end of reaction). Fast reactions were studied spectrophotometrically using a Durrum–Gibson stopped-flow spectrophotometer equipped with thermostatted 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 the reaction were displayed on a storage oscilloscope, and traces were photographed with a Polaroid camera. Values obtained from duplicate experiments were in good agreement. Reactions of chloride complexes *trans*-$[PdL_2Cl_2]$ were too fast to measure with the stopped-flow system.

RESULTS AND DISCUSSION

The isolation and characterization of several of the reaction products as bis-substituted complexes suggests that the reactions proceed according steps (3) and (4).

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The rate-determining step is therefore displacement of the first nitro-group. Pseudo-first-order spectrophotometric rate constants, k_{obs} (Table 1), when plotted against

$$trans\text{-}[PdL_2(NO_2)_2] + Y^- \xrightarrow{\text{slow}} trans\text{-}[PdL_2(NO_2)Y] + NO_2^- \quad (3)$$

$$trans\text{-}[PdL_2(NO_2)Y] + Y^- \xrightarrow{\text{fast}} trans\text{-}[PdL_2Y_2] + NO_2^- \quad (4)$$

the concentration of the nucleophile, gave straight lines with non-zero intercepts indicating that the usual two-term rate equation (5) is obeyed (k_1 arises from the

$$k_{obs} = k_1 + k_2[Y] \quad (5)$$

solvolytic path and k_2 is the second-order rate constant for bimolecular attack of Y on the substrate). Values obtained for k_2 (l mol^{-1} s^{-1}) by using a standard program of least-squares analysis on an I.B.M. 1130 computer are reported with their standard deviation in Table 2.

It is important to note that all the complexes examined exhibited nearly the same nucleophilicity sequence as that already found for platinum(II) substrates, *i.e.* $Cl^- < N_3^- < Br^- < I^- < SCN^- < (NH_2)_2CS$, in agreement with the polarization effectiveness of the donor atom of the reagent.[13] As in the case of platinum(II) complexes we now can define a set of nucleophilic reactivity constants, n_{Pd}^0, which act as a measure of the nucleophilicity of the reagent towards palladium(II). These constants are given by expression (6) using substitution reactions of the complex *trans*-[Pd(PPr$^n_3$)$_2$(NO$_2$)$_2$] as the standard. The value of k_1 used ($2{\cdot}5 \times 10^{-4}$ s^{-1}) was the mean of the intercept obtained from the

$$n_{Pd}^0 = \log \frac{k_2}{k_1/[MeOH]} \quad (6)$$

plot of k_{obs} against [Y]. The inclusion of the term [MeOH] in equation (6) serves to render the quantity in the logarithm dimensionless.

TABLE 1

First-order rate constants k_{obs} (s^{-1}) for the reactions (3) and (4) in methanol at 25 °C

L	Y	$10^2[Y]$ / M	10^2k_{obs}
AsEt$_3$	Cl$^-$	4·0	0·18
		6·0	0·23
		8·0	0·27
		10·0	0·32
		12·0	0·36
	N$_3^-$	1·0	0·28
		2·0	0·42
		5·0	0·62
		7·5	0·83
		10·0	1·04
	Br	1·0	1·12
		2·0	1·60
		4·0	2·52
		5·0	2·87
		7·5	3·83
	SCN$^-$	2·0	43·62
		4·0	81·18
		5·0	98·10
		7·5	132·7
		10·0	186·8
	CS(NH$_2$)$_2$	1·0	364·0
		2·0	605·0
		4·0	879·0
		5·0	1142
		7·5	1595
PPr$^n_3$	Cl$^-$	1·0	0·03
		2·1	0·04
		4·2	0·07
		6·3	0·09
		10·6	0·15
	N$_3^-$	1·0	0·10
		2·0	0·18
		4·0	0·36
		5·0	0·41
		7·5	0·59
		10·0	0·77
	Br$^-$	1·0	0·21
		2·0	0·36
		4·0	0·68
		5·0	0·83
		7·5	1·10
		10·0	1·50
	I$^-$	1·0	6·94
		2·0	13·53
		4·0	21·96
		5·0	27·25
		7·5	39·15
		10·0	52·61
	SCN$^-$	1·0	15·79
		2·0	32·10
		4·0	67·07
		5·0	74·62
		7·5	94·42
		10·0	129·0
	CS(NH$_2$)$_2$	1·0	275·2
		2·0	488·5
		4·0	930·0
		5·0	1483
		7·5	1934
		10·0	3066
C$_5$H$_{11}$N	Cl$^-$	1·0	71·21
		2·0	76·34
		4·0	89·30
		6·0	102·7
		8·0	117·0
		10·0	129·9
	N$_3^-$	1·0	22·68
		2·0	36·56
		4·0	74·85
		6·0	111·5
		8·0	151·0
		10·0	185·0
	Br$^-$	1·0	104·0
		2·0	145·2
		4·0	218·2
		6·0	284·5
		8·0	364·0
		10·0	441·6
	I$^-$	1·0	465·2
		2·0	998·0
		4·0	1841
		6·0	2775
		8·0	3656
	SCN$^-$	1·0	640·0
		2·0	909·0
		4·0	1460
		6·0	2110
		8·0	2590

The concentration of the substrate in the reaction mixture was always less than 5×10^{-4}M.

The values of n_{Pd}^0 are listed in Table 3, together with those of n_{Pt}^0 and n_{MeI}^0. The latter were obtained from substitution reactions of MeI in methanol at 25 °C.[10] When log k_2 values for reactions of other substrates were plotted against these calculated values of n_{Pd}^0, straight

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[13] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

lines were obtained (Figure). This indicates that palladium(II) substrates obey the linear free-energy relation (7).

$$\log k_2 = s n_{\mathrm{Pd}}^0 + \log k_1 \qquad (7)$$

The nucleophilic discrimination factor *s* is dependent on the nature of the palladium(II) complex and represents its sensitivity to changes in the nature of the entering group. The value of k_1 obtained from the intercept of the straight lines in the Figure is a measure of the intrinsic reactivity of the substrate representing a rate constant for the poorest nucleophile, *i.e.* the solvent.

TABLE 2

Second-order rate constants k_2 (l mol^{-1} s^{-1}) for the reactions (3) and (4) in methanol at 25 °C

L	Y = Cl^-	N_3^-	Br^-	I^-	SCN^-	$(NH_2)_2CS$
PPr^n_3	0·0128	0·074	0·140	4·96	12·04	303
	±0·0002	±0·006	±0·001	±0·03	±0·24	±6
$AsEt_3$	0·022	0·082	0·416		17·4	186·3
		±0·001	±0·004		±0·2	±0·3
$C_5H_{11}N$	4·32	15·8	32·2	343·7	298·6	
	±0·28	±0·1	±0·4	±5·2	±5·5	

TABLE 3

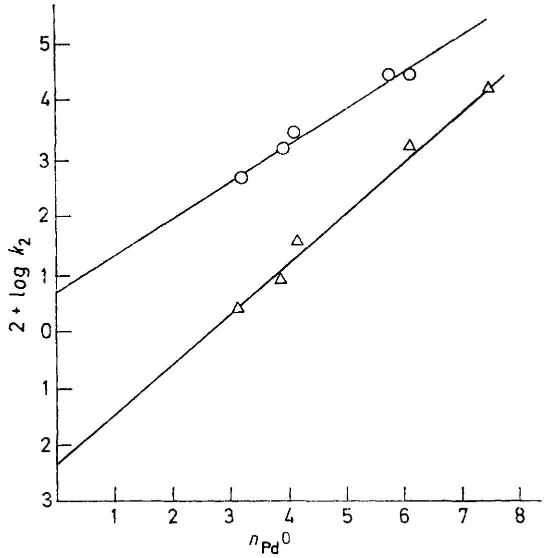
Values of nucleophilic reactivity constants n_{Pd}^0, n_{Pt}^0, and n_{MeI}^0

Y	n_{Pd}^0	n_{Pt}^0	n_{MeI}^0
Cl^-	3·13	3·04	4·37
N_3^-	3·88	3·58	5·78
Br^-	4·16	4·18	5·79
I^-	5·71	5·46	7·42
SCN^-	6·10	5·75	6·70
$(NH_2)_2CS$	7·50	7·17	7·27

The values of n_{Pd}^0 reported in Table 3 can be compared with nucleophilicity sequences given by the n_{Pt}^0 and n_{MeI}^0 values. It appears that, apart from inversion of the reactivity of I^- and SCN^-, observed in the case of the piperidine complex, there is no significant difference between the n_{Pd}^0 and n_{Pt}^0 sequences, whereas the n_{MeI}^0 values differ quite considerably. This means that factors determining nucleophilicity towards platinum(II) and palladium(II) complexes are the same, but different from those determining nucleophilicity at the carbon atom. This may be due to the different 'softness' of platinum(II) and palladium(II) with respect to carbon so that the reactivity data may be explained according to Pearson's 'hard and soft' theory.[13] In other words, it seems that both in platinum(II) and palladium(II) systems the micropolarizability of the nucleophile, *i.e.* its polarizability in the anisotropic electric field encountered in the transition state,[14] is essential in determining the reactivity, whereas it seems impossible to correlate quantitatively nucleophilic reaction rates when one takes into consideration substrates with such widely different properties as carbon and d^8 transition-metal ions.

As far as platinum(II) is concerned, thiourea is known to be a 'biphilic' reagent [14] and this is borne out in the deviation of k_2 for thiourea from the values expected on the basis of equation (6). In the systems reported here such deviations have not been observed but further information is needed to discuss this point and work is in progress on the reactivity of charged complexes. Values of *s* and k_1 for the complexes studied, calculated by means of a least-squares analysis on an I.B.M. computer **1130**, are $s = 0{\cdot}90 \pm 0{\cdot}01$ and $\log k_1 = -2{\cdot}38 \pm 0{\cdot}09$ for L = Et_3As and $s = 0{\cdot}640 \pm 0{\cdot}009$ and $\log k_1 = 0{\cdot}72 \pm 0{\cdot}06$ for L = $C_5H_{11}N$.

The different values obtained for the discrimination parameters *s* on changing L can be discussed in terms of the *cis* effect of L. The sequence 1·0 (L = PPr^n_3) > 0·9 (L = Et_3As) > 0·64 (L = $C_5H_{11}N$) can be compared with the analogous sequence obtained with platinum(II) complexes under the same experimental conditions,[8,15]



Plots of rates of reaction of palladium(II) complexes against n_{Pd}^0 for different nucleophiles: (△), *trans*-$[Pd(AsEt_3)_2(NO_2)_2]$; (○), *trans*-$[Pd(C_5H_{11}N)_2(NO_2)_2]$

i.e. 1·62 (L = PEt_3) > 1·3 (L = Et_3As) > 0·95 (L = $C_5H_{11}N$), even if the standard complex in the case of platinum(II) is *trans*-$[Pt(py)_2Cl_2]$ (py = pyridine) and the data refer to *trans*-$[PtL_2Cl_2]$ substrates. Apart from the different values of *s* in the above sequences, which can be easily due to the different nature of the leaving group and of the ligand *trans* to it, it is noteworthy that the sequences are qualitatively the same. Therefore, also in the case of palladium(II), this result can be explained by considering that ligands such as PR_3 and, to a lesser extent AsR_3, are capable of back-donation of negative charge from the metal to the ligand in the transition state. This delocalization of negative charge facilitates formation of the new bond and enhances the contribution of the nucleophile to stabilization of the transition state. As a result the rate of reaction is affected more by changing the nature of the entering group.

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