Fast Reactions at Planar Four-co-ordinate Complexes. Part II.† The Leaving-group Effect in Palladium(II) Complexes of 3-Azapentane-1,5-diamine

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The displacement of ligand X in $[Pd(3\text{-}NHpd)X]^+$ (3-NHpd = 3-azapentane-1,5-diamine) by a variety of nucleophiles Y has been studied in methanol at 25° C and I = 0·1 M (X = Cl^-, Br^-, I^-, N_3^-, or NO_2^-; Y = Cl^-, Br^-, N_3^-, I^-, SCN^-, or thiourea). The results show that, in spite of the large difference in reactivity between analogous palladium(II) and platinum(II) complexes, the lability sequence is almost the same, and, as in the case of Pt^{II} complexes, there are indications that the free-energy changes related to bond formation and weakening during the formation of the transition state are largely independent indicating that these processes are asynchronous in nature.

THE role of the nature of the leaving group in the kinetic behaviour of nucleophilic substitution processes at planar four-co-ordinate complexes of d^8 transition-metal ions has been mainly studied with platinum(II) derivatives. The data available[1,2] show that the sequences of lability for complexes differing only in the nature of the leaving group are significantly different, indicating that the mechanistic role of the leaving group is strongly dependent on the nature of the substrate examined. However, it was also pointed out that, for each substrate, the lability sequence does not depend on the nature of the entering nucleophile. This is no longer true on moving from platinum(II) to gold(III) derivatives and this difference in the kinetic behaviour has been discussed[3,4] in terms of differences in the mechanism of substitution at the complexes of the two metal ions.

As far as palladium(II) complexes are concerned, the only available data[5] refer to reactions (1) (3-NHpd = 3-azapentane-1,5-diamine) where it was possible to

$$[Pd(3\text{-}NHpd)X]^+ + am \longrightarrow [Pd(3\text{-}NHpd)(am)]^{2+} + X^- \quad (1)$$

follow kinetically the replacement of X by am by standard spectrophotometric techniques, in spite of the relatively high reactivity of the system, since pseudo-first-order conditions could be achieved by holding the concentration of the entering amine (am) in the reaction mixture constant by using buffered solutions. The use of new experimental techniques for the study of fast reactions has now allowed us to follow the processes (2) in methanol at 25 °C (X = Cl, Br, I, N_3, or NO_2; Y = Cl, Br, N_3, I, SCN, or thiourea). The results are presented in this paper and compared with those obtained from reactions of these complexes with amines and with the results of studies on the effect of the nature of the leaving group in substitutions at platinum(II) complexes.

$$[Pd(3\text{-}NHpd)X]^+ + Y^- \longrightarrow [Pd(3\text{-}NHpd)Y]^+ + X^- \quad (2)$$

EXPERIMENTAL

All the complexes examined, of the type $[Pd(3\text{-}NHpd)X][ClO_4]$ were obtained according to methods already reported in the literature[6] and characterized through their i.r. spectra[7] and elemental analysis. Methanol was purified by distillation after heating under reflux over $Mg(OMe)_2$. All other products were reagent grade.

Kinetics.—The slower reactions were followed by standard spectrophotometric techniques (Optica CF4-R double-beam recording spectrophotometer). Examination of the spectral changes with time for a thermostatted solution originally containing the starting material $[Pd(3\text{-}NHpd)X]^+$ and an excess of the entering reagent Y^- indicated, through the presence of isosbestic points, that only two complexes

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† Part I, see ref. 9.

[1] L. Cattalini in 'Inorganic Reaction Mechanisms,' ed. J. O. Edwards, J. Wiley, New York, 1970.

[2] L. Cattalini in 'Reaction Mechanism in Inorganic Chemistry,' *M.T.P. Internat. Rev. Sci., Ser.* 1, vol. 9, ed. M. L. Tobe, Butterworths, London, 1972.

[3] L. Cattalini, A. Orio, and M. L. Tobe, *J. Amer. Chem. Soc.*, 1967, **89**, 3130.

[4] L. Cattalini, M. Martelli, and G. Marangoni, *Inorg. Chem.*, 1968, **7**, 1492.

[5] A. Orio, V. Ricevuto, and L. Cattalini, *Chimica e Industria*, 1967, **49**, 1337.

[6] F. Basolo, H. B. Gray, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 4200; W. H. Baddley and F. Basolo, *ibid.*, 1966, **88**, 2944.

[7] G. N. Watt and D. S. Klett, *Spectrochim. Acta*, 1965, 1053.

are present, *i.e.* the unreacted and the substituted species. Excess of Y^- was always used to provide pseudo-first-order conditions and to force the reaction to completion {shown by comparing final spectra with those of original samples of $[Pd(3\text{-}NHpd)Y]^+$ complexes}. Fast reactions were followed by the stopped-flow method, using a Durrum–

TABLE 1

Pseudo-first-order rate constants, $k_{obs.}/s^{-1}$, for the reactions $[Pd(3\text{-}NHpd)X]^+ + Y^-$ in MeOH at 25 °C (I = 0·1M)

X	Y	$10^2[Y]/M$	$10^2k_{obs.}/s^{-1}$
NO_2	Cl^-	4	0·35
		6	0·47
		8	0·60
		10	0·73
	N_3^-	2	0·50
		4	0·87
		6	1·21
		8	1·48
	Br^-	2	0·68
		4	1·22
		6	1·70
		8	2·30
		10	2·70
	I^-	1	4·0
		2	7·9
		4	14·0
		6	21·5
		8	30
	SCN^-	1	1·53
		2	2·75
		4	5·60
		6	8·60
		8	11·6
	Thiourea	1	14
		2	32
		4	67
		6	100
		8	132
N_3	Cl^-	1	4·1
		2	5·5
		4	7·2
		6	9·4
		8	11·2
	Br^-	2	7·2
		4	11·7
		6	15·8
		8	19·5
	NO_2^-	1	3·9
		2	4·25
		4	5·8
		6	6·5
		8	8·5
	I^-	1	39
		2	64
		4	122
		6	175
		8	230
	SCN^-	1	19·5
		2	33
		4	71
		6	110
		8	142
	Thiourea	1	84
		2	162
		4	325
		6	485
		8	660
I	NO_2^-	4	25
		6	30
		8	36
		10	41
	Cl^-	4	38
		6	52
		8	62
		10	76
	Br^-	2	62
		4	87
		6	120
		8	153
		10	192
I	N_3^-	1	22
		2	32
		4	52
		6	69
		8	90
	SCN^-	1	195
		2	365
		4	750
		6	1 100
	Thiourea	0·5	440
		0·75	700
		1	870
		2	1 780
		3	2 750
Br	NO_2^-	1	59
		2	75
		4	90
		6	105
		8	125
	Cl^-	4	146
		6	182
		8	227
		10	272
	N_3^-	2	130
		4	200
		6	275
		8	350
	I^-	1	800
		2	1 350
		4	2 600
		6	4 100
		8	5 500
	SCN^-	1	650
		2	1 300
		4	2 400
		6	4 100
		8	5 300
	Thiourea	0·5	1 460
		0·75	2 100
		1	3 000
		2	5 500
		3	8 800
Cl	NO_2^-	1	75
		2	88
		4	120
		6	145
		8	175
	N_3^-	2	150
		4	225
		6	300
		8	375
	Br^-	2	240
		4	390
		6	535
		8	700
	I^-	1	765
		2	1 400
		4	2 500
		6	3 800
		8	4 800
	SCN^-	1	525
		2	1 200
		4	2 150
		6	3 550
		8	5 200
	Thiourea	0·5	1 400
		0·75	2 250
		1	3 100
		2	5 800
		3	9 500
		4	12 200

In all the kinetic runs the concentration of the complex $[Pd(3\text{-}NHpd)X]^+$ was always less than 10^{-4}M.

Gibson instrument. In all the kinetic runs the ionic strength was kept constant at 0·1M by adding the required amount of $LiClO_4$ to the reaction mixture.* Pseudo-first-order rate constants, $k_{obs.}/s^{-1}$, which are summarized in Table 1, were calculated from gradients of semilogarithmic plots of log $(D_t - D_\infty)$ against time, where D_t and D_∞ are optical densities of the reaction mixture at time t and at the end of the reaction respectively.

RESULTS AND DISCUSSION

The spectrophotometric results, and the fact that the complexes $[Pd(3\text{-}NHpd)X]^+$ can be prepared by way of metathetic exchange of the anionic ligand, are clear evidence that the processes followed kinetically are the reactions (2). As is usual in nucleophilic displacement of ligands in planar complexes of d^8 transition-metal ions, the reactions obeyed a two-term rate law of the type (3). This can be seen by plotting values of $k_{obs.}$ against $[Y^-]$ for each entering reagent and substrate.

$$\text{Rate} = (k_1 + k_2[Y])[\text{Substrate}] \qquad (3)$$

In some of the processes studied the values of k_1 were fairly low compared to those of k_2 (Table 2).

TABLE 2

First-order (k_1/s^{-1}) and second-order (k_2/l mol^{-1} s^{-1}) rate constants for the reactions (2) in MeOH at 25 °C (I = 0·1M)

		Entering reagent Y						
Leaving group		NO_2^-	Cl^-	N_3^-	Br^-	SCN^-	I^-	Thiourea
X	k_1	k_2						
Cl	0·6	14		40	80	560	630	3 100
Br	0·5	9·4	22	37		590	650	2,850
I	0·12	2·9	6·5	9·7	17·2	184		900
N_3	0·03	0·6	1·06		2·1	172	28·3	81
NO_2	10^{-3}		0·062	0·18	0·265	1·48	3·7	16·4

The nucleophilicity of the reagents Y^- towards these palladium(II) complexes is quite relevant compared with reactions at the corresponding platinum(II) complexes. On moving from $[Pt(3\text{-}NHpd)X]^+$ to $[Pd(3\text{-}NHpd)X]^+$ the corresponding second-order rate constants increase by about three orders of magnitude. However, the relative nucleophilicities of the various entering reagents Y^- are not very different for platinum(II) and palladium(II) species, as can be seen by the roughly linear relation obtained on plotting (Figure 1) values of log k_2 for attack at $[Pd(3\text{-}NHpd)Br]^+$ against corresponding values for $[Pt(3\text{-}NHpd)Br]^+$. Furthermore, the ability of the two substrates to discriminate between the various entering nucleophiles is quite similar, as can be seen in Figure 1 by the fact that the gradient of the line is not far from one, the palladium(II) complex being slightly less discriminating.

The relative lability of the group X displaced by the entering nucleophile Y^- is independent of the nature of Y and the lability sequence Cl $\simeq$ Br > I > N_3 > NO_2 qualitatively agrees with that of Cl $\simeq$ Br > I > N_3 > SCN > NO_2 obtained from reactions (1) in water at 25 °C. Even from a quantitative point of view there is a marked similarity between the two sequences. This indicates that the total charge of the transition state does not markedly affect the lability of X. In the reactions (1) and (2) (Y = thiourea) the transition state has a positive charge, whereas in all the other reactions (2) the transition state is neutral. The lability of the ligand X in the complexes $[Pd(3\text{-}NHpd)X]^+$ can also be compared with that in the platinum(II) complexes, $[Pt(3\text{-}NHpd)X]^+$. In the case of reactions (4) in water at 30 °C the lability sequence

$$[Pt(3\text{-}NHpd)X]^+ + Y^- \longrightarrow [Pt(3\text{-}NHpd)Y]^+ + X^- \qquad (4)$$

reported in the literature [8] is I $\simeq$ Br > Cl > N_3 and differs from the sequence for the palladium complexes mainly in the relative labilities of the halogens. In processes (5) in water at 25 °C the sequence of lability

$$[Pt(3\text{-}NHpd)X]^+ + py \longrightarrow [Pt(3\text{-}NHpd)(py)]^{2+} + X^- \qquad (5)$$

reported in the literature is Cl > Br > I > N_3 > SCN > NO_2 > CN which is qualitatively the same as the sequences for the palladium complexes but differs from the above sequence, again in the relative labilities of the halogens. One can conclude that, on changing the metal ion in these complexes from platinum(II) to palladium(II), the sequence of lability does not change in any drastic way, in spite of the large increase in reactivity (three orders of magnitude).

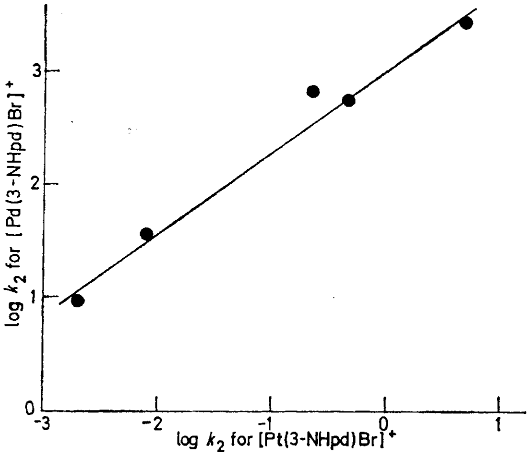

FIGURE 1 Plot of log k_2 for the complex $[Pd(3\text{-}NHpd)Br]^+$ against log k_2 values of the corresponding platinum(II) complex

* 1M = 1 mol dm^{-3}.

[8] U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, 1966, **5**, 591.

A salient feature of the substitution mechanisms of platinum(II) complexes is that when substrates differing only in the nature of the leaving group are compared, the relative lability of X is largely independent of the nature of the entering reagent Y (apart from expected deviations for 'biphilic reagents').[1,2] This fact has been discussed and interpreted[1,2] as evidence that the free-energy changes related to bond formation and weakening during asynchronous formation of the transition state are largely independent of each other. This is not true in planar four-co-ordinate gold(III) complexes and is a characteristic difference in the mechanism of displacement at these two metal ions. Both gold(III) and palladium(II) complexes are usually more reactive than platinum(II).

We can now see whether palladium(II) complexes behave more like platinum(II) or gold(III) species. In a previous paper[9] it has been shown that a nucleophilicity scale ($n_{Pd}{}^0$) can be obtained for palladium(II) complexes, and is quite similar to the $n_{Pt}{}^0$ scale for platinum(II) complexes. However, the standard substrate chosen was *trans*-[Pd(PPr$^n{}_3$)$_2$(NO$_2$)$_2$], where all the ligands are potentially biphilic, and we prefer to use an internal comparison between the data available for the complexes [Pd(3-NHpd)X]$^+$. Values of log k_2 (and log k_1, when available with sufficient precision) for each substrate and entering reagents were plotted against values of log k_2 (and log k_1) for the standard complex [Pd(3-NHpd)Cl]$^+$. In Figure 2, since data for the reaction of the standard complex with Cl$^-$ are not available, the position of Cl$^-$ in the relative nucleophilicity scale was determined by interpolation. The plots reported in Figure 2 show clearly that the relative lability of X is not affected, to any significant extent, by the nature of the nucleophile Y and we can conclude that these palladium(II) complexes, in spite of their higher reactivity which could give the impression of similarity to gold(III) species, from a mechanistic point of view behave like platinum in the sense that the substitutions occur according to an asynchronous mechanism and the free-energy changes related to bond formation and weakening during the formation of the transition state are largely independent of each other.

Finally, it seems also of interest to point out that, apart from the higher reactivity of palladium(II) as compared to platinum(II), there is another difference in the kinetic behaviour. No deviation attributable to π-interactions of biphilic ligands was observed for these palladium(II) species, at least in the limit of experimental error. The reagents NO$_2^-$ and thiourea, which are biphilic in their reaction with platinum(II), seem to behave quite normally in this case. To explain such a difference requires more data, extended also to charged substrates, to achieve a wider range of comparison.

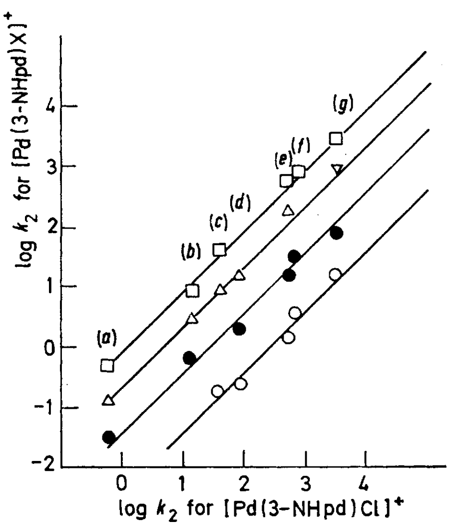

FIGURE 2 Plots of log k_2 for the complexes [Pd(3-NHpd)X]$^+$ against log k_2 values for [Pd(3-NHpd)Cl]$^+$: X = NO$_2$ (○), N$_3$ (●), I (△), and Br (□); Y = MeOH (*a*), NO$_2^-$ (*b*), N$_3^-$ (*c*), Br$^-$ (*d*), SCN$^-$ (*e*), I$^-$ (*f*), and thiourea (*g*)

We thank the Italian Council of Research (C.N.R. Rome) for support.

[4/1202 *Received*, 20*th June*, 1974]

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[9] M. Cusumano, G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1974, 490.