

## Fast Reactions at Planar Four-co-ordinate Complexes. Part 5.<sup>1</sup> The Solvent Effect on the Leaving Group in the Reactions of Neutral and Cationic Palladium(II) Complexes †

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The rate of replacement of the group X by n-propylamine or thiourea in the substrates [Pd(3-NHpd)X]NO<sub>3</sub> (3-NHpd = 3-azapentane-1,5-diamine; X = Cl, Br, I, N<sub>3</sub>, SCN, or NO<sub>2</sub>) and the equilibrium constants of some of these reactions have been studied in the solvents methanol, dimethylformamide, and dimethyl sulphoxide at 25 °C. The kinetics of substitution of the first group X, by ethylenediamine, in the substrates [Pd(L-L)X<sub>2</sub>] [L-L = 1,10-phenanthroline, 1,2-bis(diphenylphosphino)ethane, or ethylenediamine] in dimethylformamide and in some cases in methanol, at 25 °C, have also been followed. Both rate and equilibrium constants vary sensibly on going from protic to dipolar aprotic solvents. The lability sequence of the leaving group depends on the nature of the substrates and in all cases is affected to a large extent by the change in the solvent nature.

It is well established<sup>2-5</sup> that in substitution reactions at square planar complexes neither the rate of reaction nor the order of nucleophilicity of the entering group is significantly altered by change in the nature of the reaction medium. Much less is known of the solvent effect upon the leaving group. Belluco *et al.*<sup>6</sup> found that for the complexes *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>(L)X] (L = Ph or C<sub>6</sub>H<sub>4</sub>F-*m*) the relative lability of the leaving group X, *i.e.* Cl ~ I > N<sub>3</sub> ≫ NO<sub>2</sub>, does not change on going from methanol to dimethylformamide (dmf). On the other hand, during the course of our studies on the kinetic behaviour of palladium(II) square-planar complexes we noticed that for the substrates [Pd(phen)X<sub>2</sub>] (phen = 1,10-phenanthroline) the rate of substitution of the first group X by ethylenediamine (en) in the solvent dmf follows the order SCN > NO<sub>2</sub> ≫ Cl. This finding prompted us to perform a systematic investigation of the leaving-group lability in neutral and cationic palladium(II) complexes in polar and dipolar aprotic solvents.

In this paper we report the rate constants for the reactions of the substrates [Pd(3-NHpd)X]NO<sub>3</sub> [3-NHpd = 3-azapentane-1,5-diamine (diethylenetriamine, dien); X = Cl, Br, I, SCN, N<sub>3</sub>, or NO<sub>2</sub>] with n-propylamine or thiourea in dimethylformamide, dimethyl sulphoxide (dmsO), and methanol (MeOH) at 25 °C, and the equilibrium constants relative to the reactions of these substrates with the former reagent in dmf and MeOH at the same temperature. The rate constants of the reactions between the complexes [Pd(L-L)X<sub>2</sub>] [L-L = phen, 1,2-bis(diphenylphosphino)ethane (dppe), or en; X = Cl, Br, SCN, N<sub>3</sub>, or NO<sub>2</sub>] in dmf and in some cases in MeOH at 25 °C, and of the reactions of [Pd(phen)X<sub>2</sub>] (X = SCN or Cl) with en in various dmf-MeOH mixtures at 25 °C have also been determined.

### Experimental

**Materials.**—The substrates [Pd(dppe)Cl<sub>2</sub>], [Pd(en)Cl<sub>2</sub>], and [Pd(3-NHpd)X]NO<sub>3</sub> (X = Br, I, NO<sub>2</sub>, N<sub>3</sub>, or SCN) were prepared by standard methods.<sup>7-10</sup> The complexes [Pd(phen)X<sub>2</sub>] (X = Cl, Br, SCN, NO<sub>2</sub>, or N<sub>3</sub>) were prepared by mixing equimolar amounts of 1,10-phenanthroline with the appropriate salt K<sub>2</sub>[PdX<sub>4</sub>] in methanol and crystallizing the precipitates from MeOH-dmf. The complexes [Pd(dppe)X<sub>2</sub>] (X = Br, N<sub>3</sub>, SCN, or NO<sub>2</sub>) and [Pd(en)X<sub>2</sub>] (X = NO<sub>2</sub> or SCN)

were prepared from the respective dichloro-derivatives. These last substances were suspended in acetone and treated with AgPF<sub>6</sub> in the ratio 1 : 2; the precipitated AgCl was filtered off and to the solution were added two equivalents of NaX. The complexes [Pd(L-L)X<sub>2</sub>], which were obtained as crystalline precipitates on diluting the solution with water, were recrystallized from dmf-water (1 : 5). The reaction products, [Pd(dppe)(en)][BPh<sub>4</sub>]<sub>2</sub>, [Pd(phen)(en)][BPh<sub>4</sub>]<sub>2</sub>, and [Pd(3-NHpd)(NH<sub>2</sub>Pr)][BPh<sub>4</sub>]<sub>2</sub> were prepared similarly on treating the respective chloro-derivatives, suspended or dissolved in methanol depending on their solubilities, with two equivalents of AgNO<sub>3</sub>. To these solutions, after removal of the precipitated AgCl, were added two equivalents of NH<sub>2</sub>Pr or one equivalent of en, respectively when dealing with the cationic or the neutral complexes. In all cases the final products were obtained as white precipitates on addition of NaBPh<sub>4</sub> dissolved in a few drops of water. The purity of all complexes was checked by elemental analysis.

Methanol was distilled over magnesium methoxide; dmsO and dmf were distilled under reduced pressure and then stored over molecular sieves. Ethylenediamine and n-propylamine were distilled over potassium hydroxide pellets. The other products were of reagent grade.

**Kinetics and Thermodynamics.**—In order to assure pseudo-first-order conditions and to force the reactions to completion, all the kinetics were studied using at least a 10-fold excess of nucleophile with respect to the complex. The reaction course was monitored either spectrophotometrically or conductometrically. A Durrum D-110 stopped-flow apparatus equipped with a Kel-F flow system and a Radiometer CDM 3 conductivity bridge was used. The experimental details have been described elsewhere.<sup>1</sup>

The equilibrium constants were determined spectrophotometrically. The absorbance of solutions of the complexes [Pd(3-NHpd)X]NO<sub>3</sub> of fixed concentrations and at various concentrations of NH<sub>2</sub>Pr was recorded at 25 °C by means of a Cary 219 spectrophotometer equipped with a thermostatted cell holder. The ionic strength of the reaction mixture was kept constant at 0.005 mol dm<sup>-3</sup> by adding the appropriate amount of NaClO<sub>4</sub>. The equilibrium concentrations of the various species were evaluated on the basis of the absorption coefficients of the complexes [Pd(3-NHpd)X]NO<sub>3</sub> and [Pd(3-NHpd)(NH<sub>2</sub>Pr)]X(NO<sub>3</sub>). As expected for reactions in which one of the reagents is neutral, the effect of ionic strength on the rate constants proved to be negligible. Pseudo-first-order

† Supplementary data available (No. SUP 23403, 12 pp.): pseudo-first-order rate constants.

**Table 1.** Second-order rate constants  $k_2$  for reaction (1) in MeOH, dmf, and dmsO at 25 °C

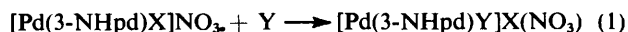
X	$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			$k_2(\text{Pd-X})/k_2(\text{Pd-I})$		
	MeOH	dmf	dmsO	MeOH	dmf	dmsO
<i>(a) Nucleophile = NH<sub>2</sub>Pr</i>						
I	15.5 ± 0.4	336 ± 13	87.6 ± 2.4	1	1	1
Br	38.1 ± 1.1	72.8 ± 0.3	64 ± 2.5	2.5	0.22	0.73
Cl	44.6 ± 1.8	18 ± 0.3	15.1 ± 0.7	2.9	0.05	0.17
SCN	2.62 ± 0.03	16.1 ± 0.2	7.98 ± 0.77	0.17	0.05	0.09
NO <sub>2</sub>	3.58 ± 0.01	22.8 ± 0.3	8.15 ± 0.53	0.23	0.07	0.09
N <sub>3</sub>	1.57 ± 0.01	3.29 ± 0.1	2.44 ± 0.09	0.1	0.01	0.03
<i>(b) Nucleophile = (NH<sub>2</sub>)<sub>2</sub>CS</i>						
I	916 ± 16 <sup>a</sup>	385 ± 7 <sup>b</sup>	120 ± 1 <sup>b</sup>	1	1	1
Br	2 890 ± 92 <sup>a</sup>	296 ± 12	61.5 ± 1.4 <sup>b</sup>	3.2	1	0.51
Cl	3 100 ± 72 <sup>a</sup>	191 ± 6	37.5 ± 1.3 <sup>b</sup>	3.4	0.5	0.31
SCN		38.5 ± 0.9			0.1	
NO <sub>2</sub>	16.9 ± 0.2 <sup>a</sup>	1.95 ± 0.07		0.02	0.01	
N <sub>3</sub>	82 ± 0.9 <sup>a</sup>	10.9 ± 0.1	3.57 ± 0.14 <sup>b</sup>	0.09	0.03	0.03

<sup>a</sup> From L. Cattalini, M. Cusumano, V. Ricevuto, and M. Trozzi, *J. Chem. Soc., Dalton Trans.*, 1975, 771. <sup>b</sup> From M. Cusumano, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Accad. Peloritana Pericolanti Sci. Fis. Mat. Nat.*, 1974, 54, 175.

rate constants,  $k_{\text{obs}}$ , which were obtained in the customary way (see Supplementary Publication), were reproducible to better than ±5%.

## Results

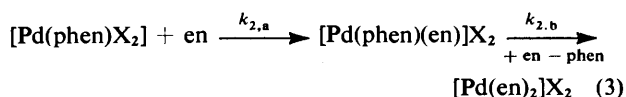
The spectral and conductivity variations with time on mixing solutions of the complexes [Pd(3-NHpd)X]NO<sub>3</sub> and n-propylamine or thiourea, as well as the nature of the reaction products, suggest that the reactions proceed according to the simple scheme (1) (Y = NH<sub>2</sub>Pr or thiourea).



The substrates [Pd(L-L)X<sub>2</sub>] (L-L = dppe or en) react with ethylenediamine according to equation (2).



In the case of the phenanthroline derivatives the ligand L-L is also replaced and the reaction scheme becomes as in (3). When X = SCN, NO<sub>2</sub>, or Br,  $k_{2,a}$  is larger than  $k_{2,b}$  and



accordingly two steps can be observed; when X = N<sub>3</sub>,  $k_{2,b}$  is larger than  $k_{2,a}$  and only one step is monitored. The value of  $k_{2,b}$ , which was determined directly from the reaction of [Pd(phen)(en)X<sub>2</sub>] with en<sup>1</sup> (84 ± 3 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), agrees well with that evaluated from the analysis of the spectral variations associated with the second step of reaction (3) (X = NO<sub>2</sub>,  $k_{2,b}$  = 83.8 ± 1.2 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>; X = SCN,  $k_{2,b}$  = 89.3 ± 2.1 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>).

When the reactions were slow enough to be followed by conductivity changes, there was good agreement between the values of  $k_{\text{obs}}$  so determined and those evaluated spectrophotometrically.

In the reactions of the complexes [Pd(3-NHpd)X]NO<sub>3</sub> and [Pd(en)X<sub>2</sub>] with amines, deprotonation of the co-ordinated ligands 3-NHpd and en by the entering amine n-propylamine or ethylenediamine, respectively, is conceivable.<sup>11</sup> Likewise, attack of ethylenediamine at the co-ordinated 1,10-phenan-

throline to form a pseudo-base<sup>12</sup> is possible in the reaction with the complexes [Pd(phen)X<sub>2</sub>]. However, neither fast conductivity changes, nor fast spectral variations associated with proton transfer or pseudo-base formation, were detected under experimental conditions identical to the kinetic ones. On this basis and owing to the fact that all the reactions proceed in one step, it has been assumed that the only reacting species are the complexes in their initial forms.

As is usual in nucleophilic substitutions of ligands in square-planar complexes, the two-term rate equation (4) was obeyed in all cases. The contribution of the solvolytic path,  $k_1$ , to the overall rate constant, could be distinguished only in some cases. The ring closure of ethylenediamine is expected

$$k_{\text{obs}} = k_1 + k_2[\text{Y}] \quad (4)$$

to be fast and, therefore, we have assumed that when Y = en  $k_2$  refers to substitution of the first group X. The values of the second-order rate constant  $k_2$  for reaction (1) are summarized in Table 1, those relative to reactions (2) and (3) in Table 2. The logarithms of the equilibrium constants for reaction (1), together with the solvent activity coefficients<sup>13</sup> log <sup>M</sup>γ<sup>d</sup> of the free anion X<sup>-</sup> at 25 °C for transfer from MeOH to dmf, are reported in Table 3.

## Discussion

The dependence of the rate constants  $k_2$  for all the reactions studied (Tables 1 and 2) on the nature of the leaving group is straightforward in the light of the well established pattern of substitution reactions at square-planar complexes.<sup>14</sup> The extent to which  $k_2$  is affected by change in the leaving group varies widely along the series of complexes examined, being largest for the phenanthroline derivatives. Furthermore, in agreement with the increasing nucleophilicity of the reaction centre,<sup>1</sup> the complexes [Pd(dppe)X<sub>2</sub>] are more reactive than [Pd(phen)X<sub>2</sub>] which in turn are more reactive than the ethylenediamine derivatives [Pd(en)X<sub>2</sub>].

The  $k_2$  values for all the reactions studied are influenced by the solvent nature. However, as is well established for substitution reactions at square-planar complexes, this solvent dependence is not large; the  $k_2$  values referring to a given reaction in two different solvents did not differ by more than a factor of 100. Nevertheless, the relative reactivity of one

**Table 2.** Second-order rate constants  $k_2$  for reactions (2) and (3) in dmf and MeOH at 25 °C

X	$10^{-5}k_2^a/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		$10^{-3}k_2^b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			$10^{-1}k_2^c/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
	dmf	MeOH	dmf	dmf-MeOH (4:1)	dmf-MeOH (1:1)	dmf
Cl	$1.21 \pm 0.06^d$	$6.42 \pm 0.21$	$0.21 \pm 0.00^d$	$0.28 \pm 0.01$	$0.33 \pm 0.02$	$1.40 \pm 0.06^d$
Br	$2.15 \pm 0.04$		$0.47 \pm 0.00$			
SCN	$6.3 \pm 0.2$	$1.33 \pm 0.04$	$17.80 \pm 0.40$	$9.1 \pm 0.05$	$2.5 \pm 0.09^e$	$3.51 \pm 0.21^f$
NO <sub>2</sub>	$3.4 \pm 0.2$	$4.7 \pm 0.2$	$2.86 \pm 0.10$			$2.8 \pm 0.17$
N <sub>3</sub>	$0.91 \pm 0.02$		$0.02 \pm 0.00$			

<sup>a</sup> L-L = dppe. <sup>b</sup> L-L = phen. <sup>c</sup> L-L = en. <sup>d</sup> From ref. 1. <sup>e</sup>  $(1.3 \pm 0.02) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in dmf-MeOH (1:4). <sup>f</sup>  $(0.77 \pm 0.07) \times 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in MeOH.

complex with respect to the others is affected by the solvent nature. This leads in some cases to changes in the lability order of the leaving group on going from one solvent to another. For the complexes  $[\text{Pd}(\text{dppe})\text{X}_2]$  for instance, passage from the protic solvent methanol to the dipolar aprotic solvent dimethylformamide leads to a decrease in the rate of substitution of the group Cl and to an enhancement in lability of the group SCN; as a result the relative lability of these groups in the two solvents is reversed. In the case of the phenanthroline derivatives the limited solubility of the complexes in methanol prevents a direct comparison of the leaving-group labilities in the two solvents; nevertheless it is possible to compare the rate constants  $k_2$  in dmf with those obtained in dmf-MeOH mixtures up to 60% MeOH. In neat dmf the group SCN is much more labile than Cl; the reactivity ratio  $k_2(\text{Pd-SCN})/k_2(\text{Pd-Cl})$  is about 85:1. On adding MeOH the rate constant for the chloro-derivative increases and that for the thiocyanato-derivative decreases; at 50% methanol the reactivity ratio  $k_2(\text{Pd-SCN})/k_2(\text{Pd-Cl})$  reduces to about 7:1. If we assume that this trend holds at higher methanol concentrations, in pure methanol the reactivity of the chloro-derivative may well be greater than that of the thiocyanate complex and solvent change will result in a reactivity inversion. In addition, it is remarkable that for these complexes the lability sequence in dmf is  $\text{SCN} > \text{NO}_2 > \text{Br} > \text{Cl} > \text{N}_3$ ; although the lability sequence depends to some extent on the system considered<sup>14</sup> it is unusual that groups such as SCN and NO<sub>2</sub> are much more labile than Br and Cl. In principle the large difference in lability of the group SCN in dmf and MeOH could be due to a different mode of bonding of the ambidentate ligand SCN to palladium(II) in the two solvents. However, i.r. studies in solution<sup>15</sup> have shown that in dmf the S-bound form is favoured; this should lead to enhanced inertness of the complexes in dmf relative to MeOH, which is not the case.

The values of the second-order rate constants for the reactions of the cationic complexes  $[\text{Pd}(3\text{-NHpd})\text{X}]^+$  both with thiourea and NH<sub>2</sub>Pr vary slightly on going from dmf to dmsO. However, the relative ease of replacement of the various groups X is not significantly dependent on the solvent. In fact, the reactivity ratios  $k_2(\text{Pd-X})/k_2(\text{Pd-I})$  (Table 1) are similar in the two solvents. If, however, we compare these values with those corresponding to methanol significant differences are observed. These differences are larger with NH<sub>2</sub>Pr as entering group; nonetheless, for both reactions, passage from the protic solvent methanol to the dipolar aprotic solvents dmf and dmsO causes an inversion in halide lability.

If the results corresponding to the various sets of complexes are examined it emerges clearly that the solvent can have a relevant effect on the relative lability of the leaving group; no lability sequence for leaving groups should be assessed unless specific reference to the reaction medium is made.

**Table 3.** Logarithms of the equilibrium constants  $K$  for reaction (1) in MeOH and dmf, and solvent activity coefficients of the free anions X<sup>-</sup> for transfer from MeOH to dmf at 25 °C

X	ln $K$		log $^M\gamma^d$
	dmf	MeOH	
Cl	7.2	9.5	6.8
Br	8.0	10.6	5.2
NO <sub>2</sub>	5.0	7.6	
SCN	8.4	7.2	3.0
N <sub>3</sub>	6.2	8.4	5.2

It is difficult to establish whether the dependence of the lability of the leaving group on the solvent nature is a ground-state or a transition-state effect. In principle, both the free-energy variation of the reactants and the free-energy variation of the transition state, consequent upon the change in solvation, can account for the variation in the rate of replacement of a given ligand in various solvents. The kinetic data here reported do not allow one to evaluate the relative importance of the two contributions; such an analysis could be accomplished only through knowledge of the Gibbs free energies of transfer of the reactants from one solvent to another.<sup>16,17</sup>

The equilibrium constants for reaction (1) are largely influenced by the solvent nature. In fact, the solvation of the reactants and products in a given system in dmf and MeOH is so different as to alter the order of the  $K$  values for the various reactions (Table 3). The solvation change of the free anion X<sup>-</sup> seems to play a major role in the overall solvation change. The largest increase in the equilibrium constants, as shown by the differences  $(\ln K_{\text{dmf}} - \ln K_{\text{MeOH}})$ , occurs with the complexes for which X = Cl, Br, or N<sub>3</sub>. Significantly, the solvation enhancement on going from dmf to MeOH is largest for the free anions Cl<sup>-</sup>, Br<sup>-</sup>, and N<sub>3</sub><sup>-</sup>, as shown by the values of the solvent activity coefficient for transfer from one solvent to the other, log  $^M\gamma^d$  (Table 3). A positive value of log  $^M\gamma^d$  means that X<sup>-</sup> is less solvated in dmf than it is in MeOH. The result that the equilibrium constant for the reaction between  $[\text{Pd}(3\text{-NHpd})(\text{SCN})]\text{NO}_3$  and NH<sub>2</sub>Pr does not increase on going from dmf to MeOH is probably due to the fact that in this case substrate solvation is also significant. For this complex, besides axial solvation, solvation of the free end of the ambidentate ligand SCN may be relevant. Thus, the solvation enhancement of the free anion SCN<sup>-</sup> on transfer from dmf to MeOH could be compensated by increase in solvation of the substrate.

#### Acknowledgements

The authors thank the Consiglio Nazionale delle Ricerche (C.N.R., Rome) for financial support.

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Received 5th April 1982; Paper 2/574