The Interaction of Aliphatic Amines with Transition-metal Complexes of Aromatic Di-imines. Part 2.[1] Concurrent Nucleophilic Attack at the Central Metal and Co-ordinated Ligand in the Reaction between Ethylenediamine and Dichloro(5-nitro-1,10-phenanthroline)palladium(II) in Dimethylformamide †

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The complex [Pd(5NO$_2$-phen)Cl$_2$] (5NO$_2$-phen = 5-nitro-1,10-phenanthroline) reacts with ethylenediamine (en) to give [Pd(en)$_2$]Cl$_2$ as a final product. This process, which occurs in several steps, has been investigated spectrophotometrically and conductometrically. Ethylenediamine attacks both palladium and co-ordinated phenanthroline to give respectively [Pd(5NO$_2$-phen)(en)]Cl$_2$ and a red adduct, which is presumably a Meisenheimer-type complex. These two substances then react with en to yield [Pd(en)$_2$]Cl$_2$. A reaction scheme for the overall process is proposed and kinetic and thermodynamic data for some of the steps are reported.

During the last decade we have studied the influence of ancillary ligands on the electrophilicity of the central metal atom in square-planar palladium(II) complexes. In particular, we have shown [2] how in substrates containing ligands such as terpyridine or phenanthroline capable of extensive π interactions the rate of replacement of a group X co-ordinated to palladium is largely enhanced with respect to the corresponding substrates with diethylenetriamine or ethylenediamine where only σ effects are exerted. Furthermore, we have shown that in the reaction between [Pd(5R-phen)Cl$_2$] (R = CH$_3$, H, Cl, or NO$_2$) and unidentate nucleophiles the rate of replacement of the first chloride increases with decreasing σ-donor power of the 5-substituted 1,10-phenanthroline (5R-phen).

With the aim of extending this work to bidentate ligands, we have studied the reaction of the above mentioned complexes with ethylenediamine (en) in dimethylformamide and found that, while when R = Cl, CH$_3$, or H the kinetic behaviour parallels that with unidentate ligands, in the case of [Pd(5NO$_2$-phen)Cl$_2$] a deep red colour is rapidly formed which subsequently fades. In this paper we report the results of a kinetic and thermodynamic investigation of the reaction between [Pd(5NO$_2$-phen)Cl$_2$] and ethylenediamine (en) in dimethylformamide at various temperatures. Kinetic data relative to the reaction of [Pd(5R-phen)Cl$_2$] (R = CH$_3$, H, or Cl) and en at 25 °C and to the reaction of [Pd(5NO$_2$-phen)(N$_3$)$_2$] with en at −30 °C are also reported.

Experimental

Materials.—The complexes [Pd(5NO$_2$-phen)X$_2$] (X = Cl or N$_3$) and [Pd(5R-phen)Cl$_2$] (R = CH$_3$, H, or Cl) were prepared as already described.[2,3] The complex [Pd(5NO$_2$-phen)(en)][ClO$_4$]$_2$ was prepared by treating [Pd(5NO$_2$-phen)(solvent)$_2$][ClO$_4$]$_2$, previously obtained in acetone from [Pd(5NO$_2$-phen)Cl$_2$] and AgClO$_4$ at room temperature, with the equivalent amount of en. The resulting solution was evaporated to dryness and the residue was crystallised from methanol.

Ethylenediamine was distilled over potassium hydroxide pellets. Dimethylformamide (dmf) was distilled under reduced pressure and then stored over molecular sieves. The other products were of reagent grade.

Kinetics.—The kinetics were studied under pseudo-first-order conditions with respect to the complex, either spectrophotometrically in the temperature range −50 to −10 °C or conductometrically in the range 20—40 °C. The experimental details have already been described.[1,2] The $k_{obs.}$ values (see SUP 56039) were reproducible to better than ±5%. Under the experimental conditions used the effect of the ionic strength proved to be negligible.

Thermodynamics.—Equilibrium constants were determined spectrophotometrically at a fixed ionic strength of 0.005 mol dm^{-3} (NaClO$_4$). The equilibrium concentration of the red adduct was evaluated on the basis of the absorbance of the reaction mixture read directly, at one wavelength in the range 400—500 nm, on the stopped-flow oscilloscope immediately after the colour-forming reaction was complete. The absorption coefficient of the adduct was evaluated from the absorbance of a mixture of the complex of known concentration and a large excess of en. In the spectral range used the absorbance of species other than the red adduct was irrelevant.

Results and Discussion

The reaction between [Pd(5NO$_2$-phen)Cl$_2$] and ethylenediamine, carried out in dmf at a variety of temperatures and reagent concentrations, leads invariably to the formation of [Pd(en)$_2$]Cl$_2$ and 5NO$_2$-phen as major final products. The reaction is accompanied by the development of a deep red colour, which subsequently, quickly fades. In addition, the conductivity of the reaction mixture, initially very low in agreement with the neutrality of the reactants, rises to a value characteristic for a 1 : 2 electrolyte in dmf.[4] The conductivity and the colour change are associated with two distinct processes, the rate constants of which could be calculated owing to the large difference in their kinetic and thermodynamic features. While the absorbance variation increases with increasing ethylenediamine concentration and decreasing temperature, the conductivity change remains constant. Furthermore, the latter process is much slower than the former. Accordingly we have determined the rate constant of the

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† *Supplementary data available* (No. SUP 56039, 6 pp.): first-order rate constants, equilibrium constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: cal = 4.184 J.

colour-forming reaction at low temperature (−50 to −20 °C) and large ethylenediamine concentration. The rate of conductivity change was easily calculated at high temperature (20—40 °C) and low en concentration, under which conditions the colour formation is almost completely absent.

The kinetic course of the processes was followed under pseudo-first-order conditions with respect to the complex. Rate equation (1) was obeyed in the case of the colour change,

$$k_{\text{obs.}} = k_2[\text{en}] \qquad (1)$$

monitored spectrophotometrically in the range 270—570 nm by low-temperature stopped-flow. The k_2 values (dm^3 mol^{-1} s^{-1}) are 171 ± 3, 278 ± 11, 376 ± 8, and 491 ± 10 at 20, 30, 35, and 40 °C (ln $k_2 = 5.36$ at 25 °C), with corresponding activation parameters of $\Delta H^\ddagger = 9.0 \pm 0.3$ kcal mol^{-1} and $\Delta S^\ddagger = -18 \pm 1$ cal K^{-1} mol^{-1}. An analogous rate equation (2) was obtained in the case of the conductivity change.

$$k_{\text{obs.}} = k_2'[\text{en}] \qquad (2)$$

The salt $[\text{Pd}(5\text{NO}_2\text{-phen})(\text{en})]\text{Cl}_2$ was the only product of the reaction between $[\text{Pd}(5\text{NO}_2\text{-phen})\text{Cl}_2]$ and ethylenediamine isolated under experimental conditions identical to the ones used to determine the rate of conductivity change. This step refers, therefore, to the reaction (3) and since the ring closure

$$[\text{Pd}(5\text{NO}_2\text{-phen})\text{Cl}_2] + \text{en} \rightleftharpoons [\text{Pd}(5\text{NO}_2\text{-phen})(\text{en})]\text{Cl}_2 \qquad (3)$$

of en is expected to be fast k_2' refers to the rate of substitution of the first Cl co-ordinated to palladium. This is confirmed by the good agreement between the k_2' value for reaction (3) at 25 °C and those of the reaction between the complexes $[\text{Pd}(5\text{R-phen})\text{Cl}_2]$ (R = CH_3, H, or Cl) and en under the same experimental conditions. For these complexes the reaction leads only to a conductivity increase, *i.e.* to the formation [2] of the species $[\text{Pd}(5\text{R-phen})(\text{en})]\text{Cl}_2$. The k_2' value for the complex under study conforms to the trend exhibited by the substrates $[\text{Pd}(5\text{R-phen})\text{Cl}_2]$, whose rate constants increase systematically but to a small extent, with decreasing σ-donor power of the substituted phenanthroline. Again, as expected for substitution reactions at square-planar complexes, the value of k_2' at 25 °C decreases by a factor of >8 on going from $[\text{Pd}(5\text{NO}_2\text{-phen})\text{Cl}_2]$ ($k_2' = 226 \pm 11$ dm^3 mol^{-1} s^{-1}) to $[\text{Pd}(5\text{NO}_2\text{-phen})(\text{N}_3)_2]$ ($k_2' = 26.7 \pm 0.5$ dm^3 mol^{-1} s^{-1}) in agreement with N_3 being a poorer leaving group with respect to Cl.

By contrast the rate of the colour-forming reaction is almost unaffected by the nature of the groups co-ordinated to palladium, the k_2 values at −30 °C being 427 ± 5 and 238 ± 12 dm^3 mol^{-1} s^{-1} respectively for $[\text{Pd}(5\text{NO}_2\text{-phen})\text{Cl}_2]$ and $[\text{Pd}(5\text{NO}_2\text{-phen})(\text{N}_3)_2]$. In addition, it is independent of the nature of the central atom. The value of k_2 for the formation of a red adduct between the complex $[\text{Pt}(5\text{NO}_2\text{-phen})\text{Cl}_2]$ and en in dmf at −40 °C (308 ± 1 dm^3 mol^{-1} s^{-1}) is very similar to that for the reaction of the analogous palladium complex (220 ± 1 dm^3 mol^{-1} s^{-1}). Moreover, none of the complexes $[\text{Pd}(5\text{R-phen})\text{Cl}_2]$ where R is a group other than NO_2 gives a colour-forming reaction. This suggests that the chromatic reaction does not involve attack at palladium but rather at co-ordinated 5-nitro-1,10-phenanthroline. The spectrum of the red adduct (see Figure), evaluated point by point from the exponential curves obtained for the colour-forming reaction, by stopped-flow is reminiscent of those of Meisenheimer complexes formed by attack of aliphatic amines at nitroaromatics.[5] The formation of these substances has been invoked by Gillard and co-workers [6,7] to explain the exceptional kinetic behaviour of transition-metal complexes containing co-ordinated nitroaromatics in their reactions with bases, on the assumption that co-ordination of di-imines to a metal centre leads to a reactivity enhancement toward nucleophiles comparable to that caused by di-imine quaternization. These proposals are very controversial [8] and the existence of 'entering nucleophile-to-co-ordinated ligand' adducts has been challenged.[9] Nonetheless we have recently found [1,3] that complexes of various transition-metal complexes of 5-nitro-1,10-phenanthroline react with bases to give red adducts. Both the spectral features, and in some cases, the rate of formation of the red adducts, are largely independent of the geometry of the complexes and of the nature of the metal. The reaction scheme assumed for the formation of Meisenheimer adducts between nitroaromatics and amines is as in equation (4). The first amine molecule attacks one of the

$$\text{nitroaromatic} + 2\ \text{amine} \rightleftharpoons \text{adduct}^- + \text{amine}^+ \qquad (4)$$

carbon atoms of the aromatic ring and the second amine molecule acts as a base abstracting a proton from the amine already bound.

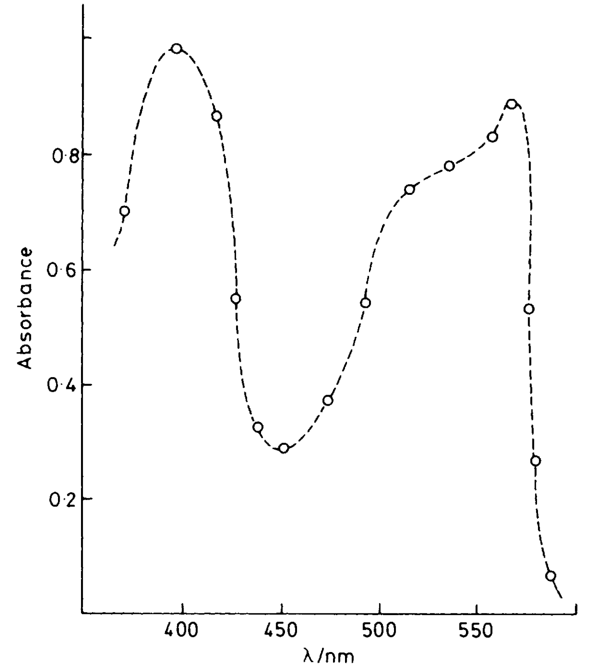
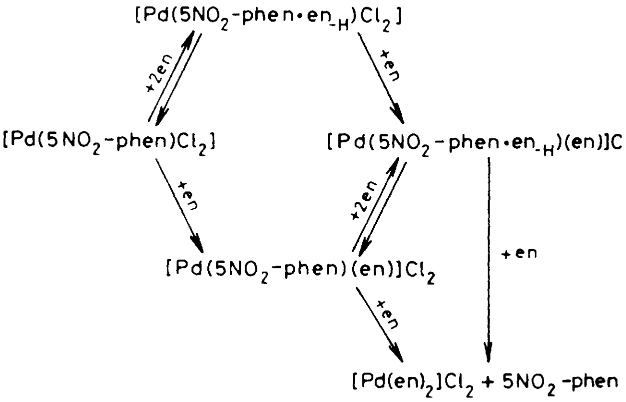


Figure. Electronic spectrum of the red transient intermediate in dimethylformamide: $[\text{Pd}(5\text{NO}_2\text{-phen})\text{Cl}_2] = 5 \times 10^{-5}$, [en] = 0.1 mol dm^{-3}; −20 °C

Our colour reaction obeys this type of stoicheiometry. In fact, we tried to evaluate an equilibrium constant for it by using the ratio [products] : [reagents] in equation (4) and obtained reasonably constant values over a five-fold range of en concentration. The average values of K evaluated at various temperatures are reported in the Table together with the corresponding thermodynamic parameters. The negative value of the formation entropy is consistent with equation (4) where the number of free particles decreases. In addition, the activation parameters, characterized by low enthalpy values and negative entropy values, are typical of reactions in which σ adducts are formed.[10] On the basis of all these considerations it is reasonable to assume that in the colour-forming reaction between $[\text{Pd}(5\text{NO}_2\text{-phen})\text{Cl}_2]$ and en a Meisenheimer complex is formed according to equation (5), where en$_{-\text{H}}$ represents

Table. Kinetic and thermodynamic parameters for the colour-forming reactions

$\frac{k_2'}{\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$	$\frac{\theta_c}{°\text{C}}$	ln k_2' at 25 °C	$\frac{\Delta H^‡}{\text{kcal mol}^{-1}}$	$\frac{\Delta S^‡}{\text{cal K}^{-1}\ \text{mol}^{-1}}$	ln K_{25}	$\frac{\Delta G^\circ}{\text{kcal mol}^{-1}}$	$\frac{\Delta H^\circ}{\text{kcal mol}^{-1}}$	$\frac{\Delta S^\circ}{\text{cal K}^{-1}\ \text{mol}^{-1}}$
(*a*) [Pd(5NO_2-phen)Cl_2]								
122 ± 5	−50	9.01	6.9 ± 0.5	−17 ± 2	0.26	−0.15 ± 0.1	−7.0 ± 0.1	−23 ± 1
220 ± 1	−40							
427 ± 8	−30							
611 ± 29	−20							
(*b*) [Pd(5NO_2-phen)(en)]Cl_2								
467 ± 9	−50	9.65	5.7 ± 0.3	−20 ± 1	2.12	−1.2 ± 0.1	−7.0 ± 0.3	−19 ± 1
770 ± 20	−40							
1 517 ± 33	−30							
2 429 ± 37	−20							



Scheme.

$$[\text{Pd}(5\text{NO}_2\text{-phen})\text{Cl}_2] + 2\ \text{en} \rightleftharpoons [\text{Pd}(5\text{NO}_2\text{-phen}{\cdot}\text{en}_{-\text{H}})\text{Cl}_2]^- + \text{Hen}^+ \quad (5)$$

ethylenediamine which has lost a proton from the nitrogen atom already bound to a carbon atom of the aromatic ring.

As already mentioned, [Pd(en)$_2$]Cl_2 is always the final reaction product between [Pd(5NO_2-phen)Cl_2] and en, independently of the temperature and en concentration, *i.e.* of the relative amounts of [Pd(5NO_2-phen)(en)]Cl_2 and [Pd(5NO_2-phen·en$_{-H}$)Cl_2]$^-$ formed in the first two concurrent steps of reaction. Both these substances, therefore, undergo further reaction with en to give [Pd(en)$_2$]Cl_2. In the reaction between [Pd(5NO_2-phen)(en)]Cl_2 and ethylenediamine either [Pd(en)$_2$]Cl_2, by replacement of 5NO_2-phen, or a red adduct, through attack at co-ordinated 5NO_2-phen, can form. Furthermore, the rate of colour fading is identical with the rate of free 5NO_2-phen formation. In fact, we observed no difference in the values of rate constants monitored at different wavelengths; while the red adduct is the only absorbing species in the range 380—580 nm, 5NO_2-phen is the only substance having a relevant absorption around 300 nm.

The Meisenheimer adduct between unco-ordinated phen and en has not been observed. This is not surprising since the formation equilibrium constant of this substance is extremely small.[1] On the basis of these considerations and in agreement with the experimental findings, an overall reaction scheme can be proposed for the reaction between [Pd(5NO_2-phen)Cl_2] and en; charges are omitted for simplicity. The replacement of 5NO_2-phen·en$_{-H}$ in [Pd(5NO_2-phen·en$_{-H}$)Cl_2]$^-$ by en to give [Pd(en)Cl_2] has been ruled out. For this last complex, the rate of replacement[2] of chloride by ethylenediamine is much slower than the observed rate for the overall process, under the same experimental conditions.

Finally we have studied the colour-forming reaction between [Pd(5NO_2-phen)(en)]Cl_2 and en, starting directly from a sample of this complex, at low temperature and high en concentration to force the reaction to completion. Both rate and equilibrium constants (Table) follow the relations (1) and (5) already found for the colour-forming reaction between [Pd(5NO_2-phen)Cl_2] and en. However, they are both larger for [Pd(5NO_2-phen)(en)]Cl_2 than for [Pd(5NO_2-phen)Cl_2]. This is probably due to the double positive charge of the former complex which enhances the electrophilicity of the metal and the carbon atoms of the phenanthroline rings with respect to the latter complex.

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Received 6*th February* 1984; *Paper* 4/207