Kinetics of Reaction of Square-Planar Complexes of Nitrosubstituted Aromatic Di-imines with Methoxide and Aliphatic Amines in Dipolar Aprotic Solvents

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Abstract

The square-planar complexes [Pt(5-NO_2phen)Cl_2], [Pd(5-NO_2phen)$_2$]$(ClO_4)_2$ and [Pd(5-NO_2phen)X_2] ($X = N_3$, Cl) give a colour forming reaction with OH^- or alkoxides in dipolar aprotic solvents. The process occurs in one observable step and the rate law is $k_{obs} = k_2$[alkoxide]. The second order rate constant k_2 is independent of the nature of the metal and of the coordinated ligands other than 5-NO_2-phen and this is taken as evidence that the nucleophilic attack does not occur at the central atom but rather at the coordinated phenanthroline to give presumably σ-adducts at the carbon. Conductivity stopped-flow shows that the colour forming reaction between neutral substrates and amines is associated with the formation of a 1:1 electrolyte. In dipolar aprotic solvents a colour forming reaction occurs also between [Pd(4-NO_2bipy)Cl_2] and bases.

Introduction

There has been much controversy [1–3] on the possibility of nucleophilic attack on polypyridines coordinated to transition metals. Over fifteen years ago Gillard [4] proposed that in complexes of polypyridines the nucleophile can attack the coordinated ligand to yield pseudo-bases and interpreted [5]** the anomalous behaviour of numerous substrates by invoking this theory. Nonetheless the existence of pseudo-bases, never proved unambiguously, has been repeatedly challenged [6, 7] and currently the problem of nucleophilic attack at the coordinated aromatic di-imine is still unsolved. We have contributed [8, 9] to this problem showing, on spectrophotometric and kinetic grounds, that in the reaction between transition metals complexes of 5-nitro-1,10-phenanthroline (5-NO_2phen) and aliphatic amines nucleophilic attack occurs both at the metal centre and coordinated phenanthroline or only at the latter, depending on the substrate and experimental conditions. In order to show that this type of process occurs also with nucleophiles other than amines and with coordinated di-imines other than 5-NO_2phen, we have extended our study to the reactions between square-planar complexes of 5-NO_2phen and OH− or alkoxides and to the reactions between [Pd(4-NO_2bipy)Cl_2] (4-NO_2bipy = 4-nitro-2,2′-bipyridine) and en or n-propylamine (n-PrNH_2). Accordingly, in this paper we report the kinetic results relative to these reactions in neat dimethylformamide (dmf) or in dimethylformamide containing 5 vol.% methanol. Kinetic data relative to a conductivity stopped-flow study of the reaction between [Me(5-NO_2phen)Cl_2] (Me = Pt or Pd) and ethylenediamine (en) in dmf and the rate constants for the reaction of [Pd(5-NO_2phen)Cl_2] with en in CH_3CN are also reported.

Experimental

The complexes [Me(5-NO_2phen)X_2] (Me = Pt or Pd; X = Cl, Br, N_3) and [Pd(5-NO_2phen)$_2$]$(ClO_4)_2$ were prepared as already described [9]. [Pd(4-NO_2-bipy)Cl_2] was prepared by reacting a water solution of K_2PdCl_4 with a methanol solution of the ligand 4-NO_2bipy [10] in a ratio 1:1. The yellow precipitate which formed immediately upon mixing the reagents was washed with water and methanol and eventually crystallized from methanol–dmf. The complex was characterized by elemental analysis and IR spectrum. The UV spectrum of a dmf solution of the complex has λ_{max} 324 (8100 mol^{-1} cm^2) and 281 nm (10000 mol^{-1} cm^2).

The solvents dmf, methanol and acetonitrile were of spectrophotometric grade and were used without further purification. The amines n-prNH_2, piperidine and ethylenediamine were distilled over KOH pellets. CH_3ONa was prepared by dissolving Na in MeOH. The concentration of the CH_3ONa solutions in the mixture dmf/MeOH was estimated by titration with HCl. To this end a fixed aliquot of the solution was properly diluted with water and then titrated with HCl using phenol red as indicator.

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In order to reduce the effect of solvolysis of CH_3ONa by dmf the solutions were prepared immediately prior to use and stored at −50 °C. It was found that within one hour the kinetic values were unaffected by aging of the solutions. NaOH was dissolved in dimethylsulphoxide or acetonitrile by the addition to the solvent of the proper amount of the crown ether 18-crown-6. The concentrations of the solutions were corrected for density change with the temperature.

The electronic spectra were recorded by means of a Perkin-Elmer Lambda 5 spectrophotometer.

The kinetics were followed at low temperature by the use of a HI-TECH SF 3 stopped-flow. The progress of the reaction was monitored either spectrophotometrically or conductometrically. In the latter case a HI-TECH CAK-401 accessory was used. In order to record a series of spectra of the reacting solutions a HI-TECH MG3/1023 rapid scanning device was used in conjunction with the low temperature stopped-flow. The kinetic runs were performed under pseudo-first-order conditions using at least a 10 fold excess of nucleophile with respect to the complex. The ionic strength was kept constant at 0.05 mol dm^{-3} by addition of the proper amount of $NaClO_4$. The k_{obs} values, which were reproducible to better than ±5%, were obtained by the analysis of the exponential curves A/t or C/t, depending on the detection system, using a HI-TECH MCS-1 data acquisition and processing system, consisting of a fast A/D converter and an Apple IIe microcomputer.

Results and Discussion

The chemical behaviour of hydroxide, methoxide or other alkoxides toward transition metal complexes of $5\text{-}NO_2$phen is very similar to that already reported [8, 9] for aliphatic primary and secondary amines. Thus, solutions of any of the $5\text{-}NO_2$phen complexes used and OH^- or CH_3O^- in dipolar aprotic solvents such as dmso, dmf or MeCN, turn immediately red–orange on mixing the substances; the colour forming reaction, which can be reversed by addition of acid, is thermodynamically unfavoured at room temperature and is exothermal. The absorption spectra of the reaction products, which are in all cases labile, are characterized by two maxima having almost the same positions and relative intensities independently of the nature of the specific substrate. This strongly suggests that the coordinated ligand $5\text{-}NO_2$phen, rather than the central metal, is involved in the process.

We have followed, by stopped-flow technique, the kinetics relative to the colour forming reaction between the complexes $[Pt(5NO_2phen)Cl_2]$, $[Pd(5\text{-}NO_2phen)X_2]$ (X = Cl, N_3) or $[Pd(5NO_2phen)_2](ClO_4)_2$ and CH_3ONa in DMF containing 5vol.% MeOH to increase the solubility of sodium methoxide. In order to reduce the rate of the reactions and at the same time to force the processes, which occur in one observable step, to completion, the temperature of the reaction mixture was maintained at −50 °C. Under pseudo-first-order conditions with respect to the complex a very simple rate law was observed

$$k_{obs} = k_2[CH_3O^-] \qquad (1)$$

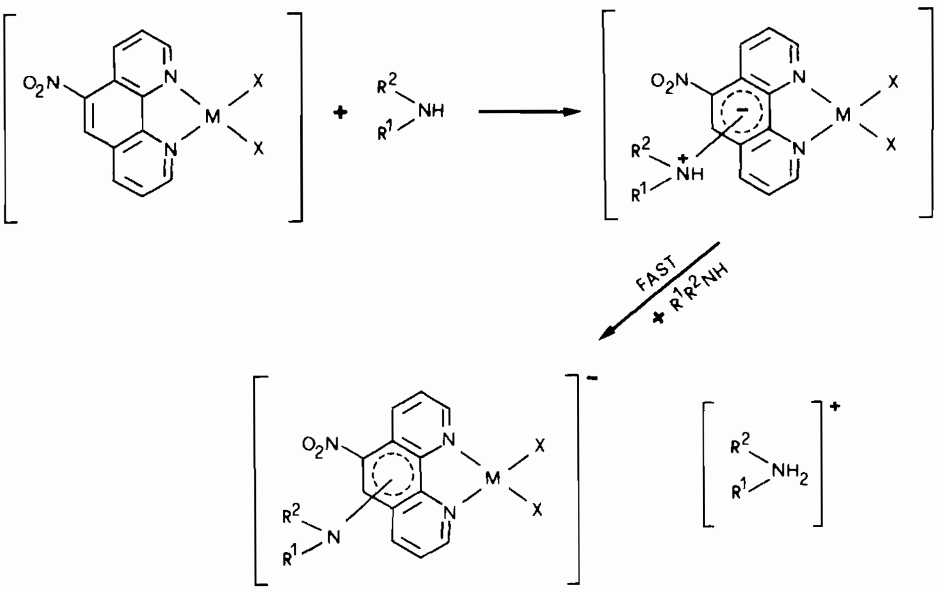
The k_2 values are reported in Table I with those relative to the colour forming reaction with ethylenediamine which occurs also in one observable step and follows, under the same experimental conditions, a rate law as in eqn. (1).

TABLE I. Second-order Rate Constants k_2 (dm^3 mol^{-1} s^{-1}) for Reaction of Complexes of $5\text{-}NO_2$phen with CH_3O^- or en in dmf–MeOH (5 vol.%)[a]

Complex	k_2 (dm^3 mol^{-1} s^{-1})	
	CH_3O^-	en
$[Pt(5\text{-}NO_2phen)Cl_2]$	6702 ± 200	52.6 ± 2
$[Pd(5\text{-}NO_2phen)Cl_2]$	5497 ± 100	44.0 ± 3
$[Pd(5\text{-}NO_2phen)(N_3)_2]$	6049 ± 400	

[a] $T = -50$ °C; $I = 0.05$ mol dm^{-3}.

As already reported [8, 9] for reaction of aliphatic amines with transition metal complexes of $5\text{-}NO_2$phen, the k_2 values are practically independent of the metal nature of the coordinated groups other than $5\text{-}NO_2$phen. Again these findings suggest that the central atom is not involved in the colour forming reaction. It is well known [11] that attack at the metal in a square-planar complex, either to give five-coordinate formation or to lead to substitution, implies dependence of the rate of reaction on the nature of the metal itself. In particular, palladium(II) complexes are 10^4 to 10^6 times more reactive than the platinum(II) analogs. In the specific case of substitution the rate of reaction should depend on the nature of the leaving group: here, however, $[Pd(5\text{-}NO_2phen)Cl_2]$ and $[Pd(5\text{-}NO_2phen)(N_3)_2]$ have comparable labilities. Finally methoxide is much more reactive than amines both toward platinum(II) and palladium(II); this reactivity order is the reverse to that usually observed in square-planar complexes [12]. On the basis of these findings, which clearly suggest nucleophilic attack at the coordinated ligand, it is reasonable to assume that in metal complexes of $5\text{-}NO_2$phen highly basic nucleophiles such as alkoxides or amines can attack the carbon atoms of the aromatic ring to give σ-adducts analogous to the Jackson–Mesenheimer [13] complexes which form in the reaction between nitro-



Scheme 1.

aromatics and bases. To date, due to their large instability and high lability, no adducts between nucleophiles and aromatic nitro-di-imines coordinated to transition metal complexes have been characterized unambiguously. Nevertheless, there are many analogies between our reactions and the formation of Mesenheimer adducts which make our assumption reasonable. The electronic spectra of the products of our reactions are reminiscent of those relative to the Jackson–Mesenheimer complexes; the kinetic and thermodynamic parameters of the two types of reaction are also very similar [2, 14]. The reaction stoichiometry, implying a ratio complex-to-nucleophile 1:1 or 1:2, respectively in the case of alkoxides and amines, is the same for both processes.

On the basis of the above reasonings the reaction between square-planar complexes of 5-NO_2phen and amines can be accounted for in terms of a mechanism in which the attack of a first amine molecule at one of the carbon atoms of the phenanthroline ring is followed by a fast proton transfer from the species formed to a second amine molecule.

In order to test the validity of this mechanism we have studied conductometrically the reaction between some neutral complexes of 5-NO_2phen and amines. Equation (2) implies increase of conductivity upon reaction. In particular, we have followed by conductivity the reactions between [Me(5-NO_2-phen)Cl_2] (Me = Pt or Pd) and ethylenediamine under pseudo-first-order conditions in dmf at –20 °C, and found that one or two conductivity changes, respectively for platinum and palladium, occur. These conductivity changes follow a first-order course and the rate law obeyed is

$$k_{obs} = k_{2,a}[\text{en}] \qquad (3)$$

The amplitude of the conductivityy changes associated with en, or other amines, is very similar for both complexes and is in turn comparable with that relative to the reaction of $[Pd(dien)Cl]^+$ (dien = diethylenetriamine) with n-prNH_2 under the same experimental conditions. This last process is known to lead to increase of the charge of the complex by one unit according to the scheme:

$$[Pd(dien)Cl]^+ + n\text{-}prNH_2 \longrightarrow [Pd(dien)(n\text{-}prNH_2)]^{2+} + Cl^- \qquad (4)$$

No conductivity change was detected on mixing [Pd(phen)Cl_2] either with n-prNH_2 or with en; it must be remembered that for the complexes with aromatic di-imines bearing no strong electron withdrawing group such as NO_2 the colour forming reaction either with amines or alkoxides does not occur.

The $k_{2,a}$ values relative to the faster conductivity change, both for [Pd(5-NO_2phen)Cl_2] ($k_{2,a}$ = 584 ± 30 dm^3 mol^{-1} s^{-1}) and for [Pt(5-NO_2phen)Cl_2] ($k_{2,a}$ = 813 ± 40 dm^3 mol^{-1} s^{-1}) are practically coincident with the k_2 values for the colour forming reactions determined by the spectrophotometric technique, respectively 611 ± 29 and 855 ± 25 dm^3 mol^{-1} s^{-1}. This indication that the colour forming reaction is associated with the formation of a 1:1 electrolyte is a confirm of the validity of eqn. (2). The slower conductivity change probably refers to the substitution of a Cl group on the adduct of the first reaction:

$$[\mathrm{Pd}(5\text{-}\mathrm{NO_2phen_{-H}}\cdot\mathrm{en})\mathrm{Cl_2}]^- + \mathrm{en} \longrightarrow [\mathrm{Pd}(5\text{-}\mathrm{NO_2phen_{-H}}\cdot\mathrm{en})(\mathrm{en})]^+ + 2\mathrm{Cl}^- \qquad (5)$$

It is interesting in this respect that only one conductivity change is observed in the case of the platinum derivative for which the substitution reaction is expected to be too slow to occur in the stopped-flow time range.

In dipolar aprotic solvents there is only a change in the rate of the colour forming reaction on going from one solvent to another. Thus in the case of the reaction between [Pd(5-NO$_2$phen)Cl$_2$] and en at –30 °C the k_2 values are 427 ± 5 and 85 ± 5 dm^3 mol^{-1} s^{-1} respectively in dimethylformamide and acetonitrile. In water, methanol or other hydroxylic solvents, however, the reaction medium has a major role on the process; the reactions between all the complexes used and aliphatic amines even at –50 °C and using a large excess of amine still lies far to the left*. In addition the spectral variations associated with the reaction in methanol are not comparable with those observed in dimethylformamide or other dipolar aprotic solvents (see Fig. 1). There is a gradual variation in the spectra of the adducts on gradually changing the reaction medium from one solvent to the other. This variation, which is fully reversible, at –50 °C, is too fast for stopped-flow on both sides. Probably the process implied proton transfer from the acidic form of the adducts to the conjugate basic form.

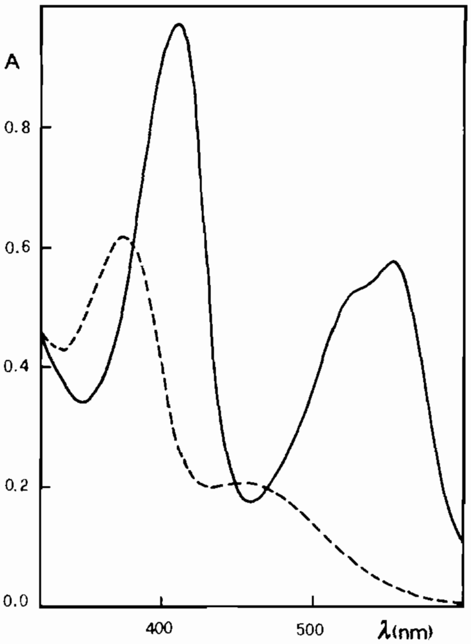


Fig. 1. Spectrum of the adduct of the reaction between [Pd-(5-NO$_2$phen)Cl$_2$] and piperidine in: – – –, MeOH; and ——, in dmf. [Complex] = 5 × 10^{-5} mol dm^{-3}.

The formation of a red adduct can also be observed, using proper experimental conditions, in the reaction between [Pd(4-NO$_2$bipy)Cl$_2$] and amines in dimethylformamide. In this particular case, however, at room temperature the red adduct is so unstable that its formation cannot be observed. Thus, at 25 °C in dmf, the reaction between [Pd(4-NO$_2$bipy)-Cl$_2$] and excess of en does not show any peculiarity and the reaction scheme is that already reported [16] for various other complexes of the type [Pd(L–L)-X$_2$] (X = Cl, Br, N$_3$, SCN, etc.; L–L = bipy, phen, en, etc.) leading to the stepwise formation of [Pd(en)$_2$]-X$_2$:

$$[\mathrm{Pd(L{-}L)X_2}] + \mathrm{en} \xrightarrow{k_a} [\mathrm{Pd(L{-}L)(en)}]\,\mathrm{X_2} \xrightarrow[+\mathrm{en};-\mathrm{L{-}L}]{k_b} [\mathrm{Pd(en)_2}]\,\mathrm{X_2} \qquad (6)$$

Both steps of reaction, performed under pseudo-first-order conditions, follow a simple rate law ($k_{obs} = k$[en]). The values of second-order rate constants k_a and k_b, respectively 291 ± 10 and 190 ± 4 dm^3 mol^{-1} s^{-1}, are directly comparable to those relative to [Pd(bipy)Cl$_2$] which are 266 ± 13 and 109 ± 4; the small increase in the reactivity of [Pd-(4-NO$_2$bipy)Cl$_2$] is probably due to the presence in the bipyridine ligand of a strong electronwithdrawing group such as NO$_2$ which increases the electrophilicity of the reaction centre. At low temperature (T = –20 °C), however, the reaction between [Pd(4-NO$_2$bipy)Cl$_2$] and en show new features. Though the final product is still [Pd(en)$_2$]-Cl$_2$, the process is associated with the fast formation of a red labile intermediate. This colour forming reaction is reversed by addition of acid; the electronic spectrum of the transient recorded by rapid scanning spectrophotometry, is characterized by a large absorption in the visible region (Fig. 2). No colour

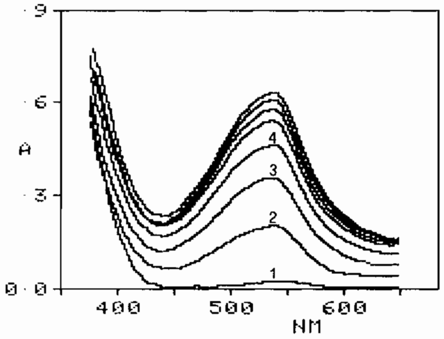


Fig. 2. Spectral variations in time for the reaction between [Pd(4NO$_2$-bipy)Cl$_2$] and en in dmf. T = –50 °C; Δt = 200 ms; [Complex] = 5 × 10^{-5} mol dm^{-3}; [en] = 0.5 mol dm^{-3}.

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*It is interesting in this respect that for nitroaromatics the stability of the σ-adducts with bases is dramatically reduced [15] on going from dipolar aprotic solvents to protic solvents.

forming reaction is observed in the complex with unsubstituted bipyridine even at the lowest temperature which can be reached in dmf ($\simeq -50$ °C). In this respect the chemical behaviour of these substrates parallels that relative to complexes with phenanthrolines where only the nitrosubstituted form leads to a colour forming reaction with bases. Finally it is interesting to note that NO_2 is not the only electron withdrawing group which causes the formation of labile coloured adducts. Other research groups [17] have also reported colour forming reactions between nucleophiles and complexes of di-imines bearing cyano or sulphonato groups.

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