The Effect of Co-ordination on the Rate of Methoxydechlorination of 5-Chloro-1,10-phenanthroline

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The kinetics of methoxydechlorination of 5-chloro-1,10-phenanthroline when co-ordinated to Ni^{II}, Ru^{II}, and Os^{II} have been studied in dimethyl sulphoxide–methanol (89.9 : 10.1 w/w). In all cases studied there is a considerable enhancement of reactivity which bears more relationship to the total charge on the complex than it does to the nature of the central metal ion. The following complexes have been examined (relative rates at 25 °C in parentheses: $[Ru(5\text{-}Cl\text{-}phen)_3]^{2+}$ (5 420), $[Ni(5\text{-}Cl\text{-}phen)_3]^{2+}$ (3160), $[Os(5\text{-}Cl\text{-}phen)_3]^{2+}$ (2 680), $[Os(5\text{-}Cl\text{-}phen)_2(acac)]^+$ (353); $[Os(5\text{-}Cl\text{-}phen)_2(ox)]^\circ$ (95), and 5-Cl-phen (1). This is in contrast to the *N*-alkyl compounds which add methoxide in the 2-position and are deactivated towards methoxydechlorination.

1,10-PHENANTHROLINE forms many complexes with a wide range of metal ions and these complexes, as well as those of suitably substituted phenanthrolines, make ideal substrates for the study of the effect of co-ordination on aromatic reactivity. Some years ago we examined the nitration of 1,10-phenanthroline when co-ordinated to cobalt and iron [1,2] and, since the nitration of free and co-ordinated phenanthroline occurs at the 5-position, we extended our studies to the effect of co-ordination on nucleophilic substitution of aromatic co-ordinated ligands and examined the kinetics of the displacement of chloride from 5-chloro-1,10-phenanthroline.[3] In view of the renewal of interest in this type of reaction [4,5] we are reporting our findings in detail. The reactions of the free ligand are described in the preceding paper.[6]

RESULTS

Tris(5-*chloro*-1,10-*phenanthroline*)*ruthenium*(II) *Perchlorate*.—$[Ru(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$, like the previously studied $[Ru(phen)_3]^{2+}$ species,[7] is inert to ligand substitution. In the presence of sodium methoxide in dimethyl sulphoxide–methanol (89.9 : 10.1 w/w) chloride ions are released but, even at the end of the reaction, there is no detectable amount of unco-ordinated substituted phenanthroline in the solution. The final titre of free chloride is exactly that calculated for complete replacement of the bound chlorine. The reaction product was precipitated by diluting the solution with an equal volume of ethanol and adding a large excess of diethyl ether. The dried product, dissolved in dimethyl sulphoxide, has a ^1H n.m.r. spectrum fully consistent with that expected for tris(5-methoxy-1,10-phenanthroline)-ruthenium(II) perchlorate, with an aromatic proton multiplet in the region τ 0.7—2.2 and a singlet assigned to the methoxy protons at τ 5.66, the peak areas being in the ratio 7 : 3. Combustion analysis of the perchlorate was unsuccessful owing to its explosive nature, but the iodide salt, $[Ru(5\text{-}MeO\text{-}phen)_3]I_2$, into which it was converted, gave a satisfactory analysis.

The release of chloride was studied in the presence of at least a ten-fold excess of methoxide and follows a first-order rate law. Plots of $\ln([Cl^-]_\infty - [Cl^-]_t)$ against time ($[Cl^-]_t$ and $[Cl^-]_\infty$ are the titres at time t and at the end of the reaction, respectively) are linear for at least two half-lives. The first-order rate constants are collected in Table 1.

TABLE 1

Rate constants for the methoxydechlorination of co-ordinated 5-chloro-1,10-phenanthroline in 89.9 : 10.1 w/w dimethyl sulphoxide–methanol

Complex	t/°C	$[MeO^-]$/ M	$[MeO^-]_{eff}$/ M	10^3k_{obs}/ s^{-1}
$Ru(5\text{-}Cl\text{-}phen)_3^{2+}$	6.9	0.049	0.063 [a]	0.053
		0.100	0.160	0.097
		0.176	0.362	0.163
		0.250	0.63	0.218
		0.312	0.90	0.258
		0.355	1.11	0.285
	15.6	0.048	0.062 [b]	0.193
		0.100	0.164	0.32
		0.152	0.30	0.42
		0.233	0.58	0.57
	25.0	0.025	0.029 [c]	0.33
		0.065	0.094	0.67
		0.100	0.169	1.03
		0.187	0.43	1.55
$Os(5\text{-}Cl\text{-}phen)_3^{2+}$	25.0	0.071	0.106 [c]	0.39
		0.100	0.168	0.51
		0.150	0.30	0.73
		0.197	0.47	0.88
		0.261	0.73	1.09
		0.293	0.88	1.19
$Os(5\text{-}Cl\text{-}phen)_2(acac)^+$	25.0	0.100	0.168 [c]	0.067
		0.290	0.87	0.183
$Os(5\text{-}Cl\text{-}phen)_2(ox)$	25.0	0.100	0.168 [c]	0.018
	40.0	0.055	0.078 [d]	0.055
		0.100	0.176	0.103
		0.181	0.429	0.177
		0.248	0.71	0.272
		0.304	1.00	0.35
	55.0	0.100	0.183 [e]	0.61
$Ni(5\text{-}Cl\text{-}phen)_3^{2+}$	7.4	0.057	0.077 [a]	0.035
		0.100	0.160	0.056
		0.142	0.263	0.073
		0.215	0.49	0.137
		0.257	0.65	0.192
		0.300	0.84	0.257
	18.2	0.100	0.165 [f]	0.255
	25.0	0.057	0.079 [c]	0.38
		0.100	0.169	0.60
		0.142	0.280	0.88
		0.201	0.48	1.40

[a] Using $\alpha = 6.01$. [b] $\alpha = 6.41$. [c] $\alpha = 6.86$. [d] $\alpha = 7.56$. [e] $\alpha = 8.26$. [f] $\alpha = 6.53$.

Tris(5-*chloro*-1,10-*phenanthroline*)*osmium*(II) *Perchlorate*.—The chemistry of this complex in the presence of methoxide in the DMSO–MeOH solvent mixture is very similar to that of the Ru^{II} complex. There was no evidence for any ligand displacement even after several days at 55 °C. The chloride is stoicheiometrically displaced from the ligand and the reaction product was isolated in the same way as the analogous Ru^{II} species and identified as $[Os(5\text{-}MeO\text{-}phen)_3][ClO_4]_2$ by its ^1H n.m.r. spectrum. The displacement of chloride follows a first-order rate law with linear semi-logarithmic plots for at least two half-lives. The first-order rate constants are collected in Table 1.

Acetylacetonatobis(5-*chloro*-1,10-*phenanthroline*)*osmium*(II) *Perchlorate*.—This complex is only slightly soluble in the DMSO–MeOH solvent mixture but there was no evidence for the displacement of the substituted phenanthroline ligands even after several days at 55 °C in the presence of 0.1M-NaOMe. The reaction product, isolated as its bromide, has a ^1H n.m.r. spectrum that contains indistinct peaks assigned to the aromatic protons, a singlet at τ 4.51 (1) (acetylacetonate methine proton), a singlet at τ 5.35 (6) (methoxy protons), and a singlet at τ 7.7 (6) (methyl protons of acetylacetonate) (the relative areas under the peaks are in parentheses). This demonstrates clearly that the acetylacetonate ligand also remains bound to the osmium throughout the reaction. The chloride release was studied in the usual way but the low solubility of the substrate required titration with 2×10^{-3}M-$AgNO_3$ and the results are therefore less precise. The first-order rate constants are collected in Table 1.

Bis(5-*chloro*-1,10-*phenanthroline*)*oxalato-osmium*(II). —The solubility of this complex in the solvent mixture is also rather low and all studies had to be made with dilute solutions. The phenanthroline ligand remains bound throughout the reaction and it seems likely that the oxalate also remains bound although there is no direct evidence for this. The semi-logarithmic plots were linear for at least two half-lives and the first-order rate constants are collected in Table 1.

Tris(5-*chloro*-1,10-*phenanthroline*)*nickel*(II) *Perchlorate*.—The study of this complex is complicated by the fact that the bidentate ligands are displaced from the nickel at rates that are similar to those of methoxydechlorination. Using the semi-quantitative colorimetric test for the free ligand, it can be shown that, whereas the test is negative shortly after mixing the solutions of complex and methoxide, *ca.* 20% of the ligand has been displaced after 100 h at 25.0 °C in the presence of 0.10M-NaOMe and this concentration remains constant thereafter. The equilibrium was not studied in detail and so it is not known whether species containing less than two substituted phenanthrolines bound to the nickel are present in any significant amount, nor whether the vacated co-ordination sites are occupied by methanol, methoxide, or dimethyl sulphoxide. However, the absence of solvolysis when no sodium methoxide is added and a dependence of the amount of free substituted phenanthroline species on the concentration of methoxide, would suggest that at least one methoxide is co-ordinated. It is therefore reasonable to believe that the nickel(II) species containing less than three phenanthroline type ligands will carry lower charges than the original substrate and, in view of the results obtained for the Os^{II} complexes, will be less reactive towards methoxydechlorination. The less basic 5-chloro-1,10-phenanthroline[8] is likely to be a much poorer ligand than the 5-methoxy-product and should be displaced in preference to the latter. As a consequence of these effects the observed first-order rate constant for the release of chloride will not remain constant and will decrease as the reaction proceeds. In addition, the experimentally determined ' infinity ' titre will be less than that calculated for three chlorines per mole of complex present. This was indeed observed. The experimentally determined ' infinities,' in terms of moles of free chloride present per mole of complex after ten half-lives, are collected in Table 2. The plots of $\ln([Cl^-]_{calc} - [Cl^-]_t)$ against time (where $[Cl^-]_{calc} = 3[complex]_{initial}$) are curved, the slopes becoming less negative as the reaction proceeds, and the first-order rate constants collected in Table 1 are the initial slopes of these plots.

TABLE 2

Equivalents of chloride released at the completion of the methoxydechlorination of $[Ni(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$ in dimethyl sulphoxide–methanol (89.9 : 10.1% w/w) at 7.4 °C[a]

$[MeO^-]$	0.057	0.100	0.142	0.215	0.257
Equivalents $[Cl^-]$/mol	2.91	2.70	2.59	2.38	1.94

[a] If the reaction mixture is kept in a sealed tube at 120 °C for 30 min 3.0 equivalents are released.

In view of the reversibility of the binding of the phenanthrolines to nickel(II), the catalytic role of small quantities of nickel(II) perchlorate, added to a solution of 5-chloro-1,10-phenanthroline and 0.10M-NaOMe in the DMSO–methanol mixture, was examined. There was no evidence for any acceleration of the rate of release of chloride and it is likely that the catalyst is soon sequestered by the reaction product.

Tris(5-*chloro*-1,10-*phenanthroline*)*iron*(II) *Perchlorate and Tris*(5-*chloro*-1,10-*phenanthroline*)*cobalt*(III) *Perchlorate*.—Addition of sodium methoxide to solutions of these complexes in the solvent mixture causes rapid decomposition and the 5-chloro-1,10-phenanthroline was completely displaced before the first sample could be taken (15—30 s). No free chloride ions could be detected in solution and it was concluded that the ligand was displaced before it could react significantly with methoxide. The base-catalysed displacement of chelating diimine ligands from Fe^{II} is well established[9-11] but Co^{III} amine complexes are generally substitutionally inert. However, electron transfer between $[Co(phen)_3]^{2+}$ and $[Co(phen)_3]^{3+}$ is reasonably fast[12] and traces of Co^{II} might catalyse the act of ligand substitution. Margerum and Morgenthaler[13] have reported that the base hydrolysis of $[Co(phen)_3]^{3+}$ in aqueous solution is catalysed by traces of $[Co(phen)_3]^{2+}$. Nevertheless, twelve-fold recrystallisation of $[Co(5\text{-}Cl\text{-}phen)_3][ClO_4]_3$ from water did not lead to any significant decrease in its substitution lability.

DISCUSSION

The complexes that have been studied fall into three categories depending upon their relative reactivities towards methoxydechlorination and ligand substitution. Category (1) contains those complexes in which methoxydechlorination is complete before there is any measurable displacement of the substituted phenanthroline, *e.g.* $[Ru(5\text{-}Cl\text{-}phen)_3]^{2+}$, $[Os(5\text{-}Cl\text{-}phen)_3]^{2+}$, $[Os(5\text{-}Cl\text{-}phen)_2(acac)]^+$, and $[Os(5\text{-}Cl\text{-}phen)_2(ox)]$. Category (2) contains those complexes which lose their ligands at rates that are comparable with that of methoxydechlorination, *e.g.* $[Ni(5\text{-}Cl\text{-}phen)_3]^{2+}$, and category (3) contains the useless complexes that lose their ligands before any significant amount of methoxydechlorination has taken place. Although the reactions of category (2) complexes can give useful semi-quantitative information provided one limits the study to a measurement of initial rates, only those of the category (1) complexes can be studied in depth. All the reactions of the complexes of this category followed strictly first-order rate laws for at least two half-lives at fixed methoxide concentrations, provided these were sufficiently large compared to that of the co-ordinated ligand. The experimentally determined final concentration of ionic chloride agreed closely with the values calculated for complete displacement of chloride from the ligand. This behaviour clearly indicates that methoxydechlorination of one ligand in the complex has no significant effect upon the reactivity of the remaining ligands. The rate constant obtained from the slope of the semi-logarithmic plot is already statistically corrected for the number of ligands in the complex.*

The rate is also dependene upon the concentration of methoxide but plots of k_{obs} against $[MeO^-]$ are not linear (Figure 1). In the cases of $[M(5\text{-}Cl\text{-}phen)_3]^{2+}$ (M = Ru or Os) and $[Os(5\text{-}Cl\text{-}phen)_2(acac)]^+$, the slope decreases with increasing $[MeO^-]$, while with $[Os(5\text{-}Cl\text{-}phen)_2(ox)]$ and $[Ni(5\text{-}Cl\text{-}phen)_3]^{2+}$ the curvature is in the opposite direction. It is to be noted that the departure from a first-order methoxide dependence of the rate of methoxydechlorination of the free ligand at 63.9 °C is much more marked than any of these and takes the form, $k_{obs} = (k_2^0 + k_2'[MeO^-])[MeO^-]$, which can be rearranged to give $k_2 = k_2^0\ (1 + \alpha[MeO^-])$, where $k_2 = k_{obs}/[MeO^-]$, and $\alpha = k_2'/k_2^0$.[6] This deviation was explained in terms of a medium effect brought about by inadequate amounts of methanol to solvate fully the methoxide when the latter is present at high concentration. When varying the concentration of methoxide no attempt was made to maintain constant ionic strength and so it is possible that the charged substrates might be subject to a negative salt effect, not present in the reaction of the uncharged ligand. Addition of $LiClO_4$ (final concentration of 0.142M) reduces the observed rate constant at 0.1M MeO^- by a factor of three in the reaction of the $[M(5\text{-}Cl\text{-}phen)_3]^{2+}$ (M = Ru or Os) complexes. Since it was not possible to obtain $LiClO_4$ free of water it is possible that this effect arises from the addition of water. The ionic strengths are too large and the dielectric constant of the medium too small for activity coefficients to be calculated by any simple expression and so it is impossible to say whether or not the difference in behaviour has the magnitude or direction of a primary salt effect.

In order to examine the form and magnitude of the deviations we have assumed that the medium effects can be encompassed by the departure of the rate of methoxydechlorination of the free ligand from a first-order dependence on $[MeO^-]$ and wish to introduce the quantity $[MeO^-]_{eff}$, defined by $[MeO^-]_{eff} = k_{obs}/k_2^0$, *i.e.* the effective methoxide concentration is that quantity by which the observed first-order rate constant for the methoxydechlorination of the free ligand must be divided by in order to obtain a concentration independent second-order rate constant k_2^0. Clearly, the value of $k_{obs}/[MeO^-]$ approaches k_2^0 as $[MeO^-]$ approaches zero and, equally clearly, if the reactions of the co-ordinated ligands were subject to the same medium effects as the free ligand, plots of k_{obs} against $[MeO^-]_{eff}$ would be linear and pass through the origin. By combining the equation defining $[MeO^-]_{eff}$ with the observed empirical dependence of k_{obs} for the free ligand on $[MeO^-]$ it can be shown that $[MeO^-]_{eff} = (1 + \alpha[MeO^-])[MeO^-]$. Unfortunately, because of the large difference between the reactivities of the free and co-ordinated ligand, the free ligand was only studied in detail at 63.9 °C while some of the more reactive complexes were studied at temperatures as low as 7 °C. An accurate value of α was obtained from a least-squares analysis of the data at 63.9

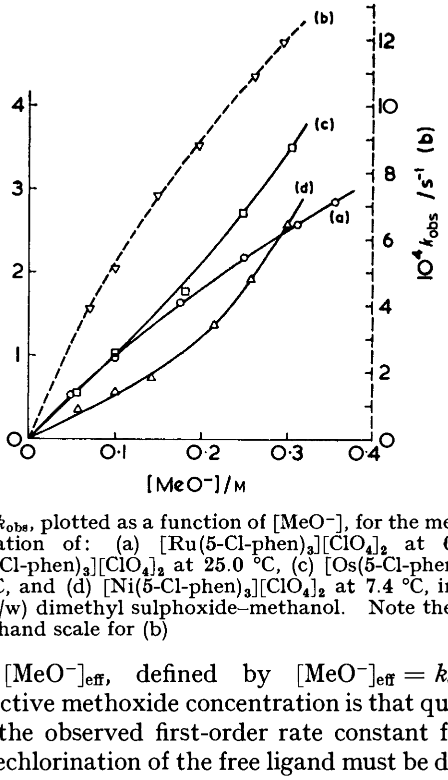

FIGURE 1 k_{obs}, plotted as a function of $[MeO^-]$, for the methoxydechlorination of: (a) $[Ru(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$ at 6.9 °C, (b) $[Os(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$ at 25.0 °C, (c) $[Os(5\text{-}Cl\text{-}phen)_2(ox)]$ at 40.0 °C, and (d) $[Ni(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$ at 7.4 °C, in 89.9 : 10.1% (w/w) dimethyl sulphoxide–methanol. Note the use of the right-hand scale for (b)

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* For a reaction sequence, $AX_n \xrightarrow{k_n} AX_{n-1} + X^-$ for $n = 1,2\,.\,.\,N$, $d[X^-]/dt = \sum_1^N k_n[AX_n]$. If $k_n = nk_1$ then $d[X^-]/dt = k_1 \sum_1^N n[AX_n] = k_1[X]_{bound}$. If the reaction goes to completion, $[X]_{bound} = [X^-]_\infty - [X^-]_t$. Therefore $\ln([X^-]_\infty - [X^-]_t) = k_1t + c$.

°C and less accurate values were obtained for the other temperatures where data are available. The values of α used to determine $[MeO^-]_{eff}$ at the temperatures where the complexes were studied were obtained by interpolation or extrapolation of the linear plot of ln α *versus* $1/T$. These values are given in Table 1. The plots of k_{obs} *vs.* $[MeO^-]_{eff}$ are shown in Figure 2 where it will be seen that, while those for $[Ni(5\text{-}Cl\text{-}phen)_3]^{2+}$ are linear (with a finite intercept for the data obtained at 25.0 °C) the rest are curved with slopes that decrease as $[MeO^-]_{eff}$ increases. Only in the cases of $[Ru(5\text{-}Cl\text{-}phen)_3]^{2+}$ at 6.9 °C, $[Os(5\text{-}Cl\text{-}phen)_3]^{2+}$ at 25.0 °C, and $[Os(5\text{-}Cl\text{-}phen)_2(ox)]$ at 40.0 °C are there sufficient data points to make analysis of the curves worthwhile and in all cases plots of k_{obs}^{-1} against $[MeO^-]_{eff}^{-1}$ are linear with a positive intercept, indicating a relationship of the form, $k_{obs} = a[MeO^-]_{eff}(1 + b(MeO^-]_{eff})^{-1}$. If this relationship has any significance, the constant a can be identified as k_2^0 for the co-ordinated ligand and serve as a basis for the comparison of the individual complexes after correction for medium effects. Unfortunately, adequate studies of the dependence of k_{obs} on $[MeO^-]$ are not available over a wide enough range of temperature to allow interpolation or extrapolation to a common temperature, say 25 °C.

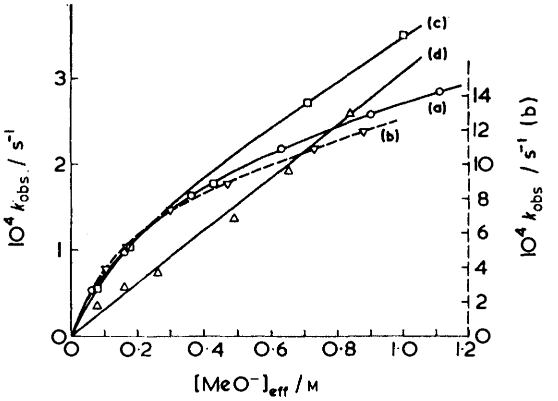

FIGURE 2 k_{obs}, plotted as a function of $[MeO^-]_{eff}$ for the methoxydechlorination of: (a) $[Ru(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$ at 6.9 °C, (b) $[Os(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$ at 25.0 °C, (c) $[Os(5\text{-}Cl\text{-}phen)_2(ox)]$ at 40.0 °C, and (d) $[Ni(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$ at 7.4 °C, in 89.9—10.1% (w/w) dimethyl sulphoxide–methanol. Note the use of the right-hand scale for (b)

Since the purpose of this investigation was to examine the effects of co-ordination on the reactivity of ligands and since it can be seen by inspection that these effects are considerable, it is important not to be sidetracked by problems that are, as yet, unresolved. We shall, therefore, compare reactivities under conditions that are as closely matched as possible. In Table 3 we compare k_{obs} values for a constant $[MeO^-]$ (0.100 mol dm^{-3}) which, with the exception of the rate constant for the reaction of the free ligand, which was obtained by extrapolation, were measured experimentally at 25.0 °C. The coefficients, $k_{obs}/[MeO^-]_{eff}$ are also listed but only in the case of the free ligand is this equal to k_2^0. It is clear that, where the relationship $k_{obs} = a[MeO^-]_{eff}(1 + b[MeO^-]_{eff})^{-1}$ is followed, $k_{obs}[MeO^-]_{eff}$ will be less than a but, since b lies within the range 1—3 mol dm^{-3}, in none of the cases listed in Table 3 will $k_{obs}/[MeO^-]_{eff}$ be less than 60% of a when $[MeO^-] = 0.10$ mol dm^{-3}.

The most important conclusion to be drawn from the data in Table 3 is that, in the three tris complexes $[M(5\text{-}Cl\text{-}phen)_3]^{2+}$ (M = Ru, Os, or Ni), the ligand is some 3 000—5 000 times more reactive than when it is unco-ordinated. This effect swamps the much smaller difference between the three complexes and the even smaller ambiguity arising from the choice of method used in making the comparison. The change in reactivity on going from $[Os(5\text{-}Cl\text{-}phen)_3]^{2+}$ to $[Os(5\text{-}Cl\text{-}phen)_2(acac)]^+$ and $[Os(5\text{-}Cl\text{-}phen)_2(ox)]$, which covers a factor of 30, indicates that the reactivity of the co-ordinated ligand is affected by the nature of the other ligands present in the complex. The fact that the replacement of the chlorine in the 5-position by methoxide in one ligand does not affect the reactivity of the others in spite of its considerable effect upon the basicity of the nitrogen [8] suggests that electron displacement changes resulting from the different donor powers of the ligands are not a major cause of the change in reactivity.

TABLE 3

A comparison of the reactivity towards methoxydechlorination of free and co-ordinated 5-chloro-1,10-phenanthroline in dimethyl sulphoxide–methanol (89.9 : 10.1% w/w) at 25.0 °C

Complex	$10^3 k_{obs}/s^{-1}$ for $[MeO^-]_{st}$ = 0.01M	Relative rate	$10^3 k_{obs}/[MeO^-]_{eff}/$ l mol^{-1}
$Ru(5\text{-}Cl\text{-}phen)_3^{2+}$	1.03	5 420	6.1
$Os(5\text{-}Cl\text{-}phen)_3^{2+}$	0.51	2 680	3.1
$Ni(5\text{-}Cl\text{-}phen)_3^{2+}$	0.60	3 160	3.5
$Os(5\text{-}Cl\text{-}phen)_2(acac)^+$	0.067	353	0.40
$Os(5\text{-}Cl\text{-}phen)_2(ox)$	0.018	95	0.107
5-Cl-phen	0.000 19 [a]	1	0.0011

[a] From data in ref. 6.

It is possible to argue that the change of ligand affects the π-donor ability of the osmium. Evidence has been presented to suggest that d^6 ions in oxidation state (+II), *e.g.* low-spin Fe^{II} and Ru^{II}, can act as π-donors to heterocyclic amine ligands [14,15] and there is no reason to believe that their congener, Os^{II}, will behave differently. Such 'back donation' should reduce nucleophilic reactivity since it will disfavour the delocalisation of the negative charge brought into the transition state by the entering nucleophile. Reduction in the number of substituted phenanthrolines will allow stronger 'back donation' to the remainder. This might account for the reduced reactivity of $[Os(5\text{-}Cl\text{-}phen)_2(ox)]$ but there is evidence to suggest that the acetylacetonate ligand is a better π-acceptor than phenanthroline; for example, the magnetic properties of low-spin, d^5, tris-chelated Ru^{III} complexes indicate that, while the odd t_{2g} electron remains on the metal in the tris-1,10-phenanthroline complex, it is significantly delocalised over the ligands in the tris-acetylacetonato complex.[16] One might infer that, if conjugative effects of this sort were dominant,

$[Os(5\text{-}Cl\text{-}phen)_2(acac)]^+$ would be more reactive than $[Os(5\text{-}Cl\text{-}phen)_3]^{2+}$.

Therefore, we conclude that the major effect responsible for the activation of the ligand is the stabilisation of the negative charge that develops in the transition state by the positive charge of the metal ion. This effect is reduced when anionic ligands are introduced into the complex but it is clear that the dinegative oxalato ion does not fully cancel out the effect of the dipositive charge on the metal. Co-ordination differs from *N*-alkylation where the positive charge, now essentially centred on the nitrogen, discriminates in favour of nucleophilic attack at the 2-position.

In view of the current revival of interest in the formation of ' pseudo base ' adducts of *N*-heterocyclic ligands when bound to transition metals[4,5] it is necessary to make some comment about the difference in behaviour of the free ligand and the complexes in respect to the dependence of rate upon the concentration of methoxide. The difference between the $[Ni(5\text{-}Cl\text{-}phen)_3]^{2+}$ cation and the other tris species might be more apparent than real and due to errors arising from the competition between the substitution of chloride and the displacement of the ligand. However, these errors are likely to lead to rate constants that are too low rather than too high and are most serious at the higher methoxide concentrations. The curvature of the plots in Figure 2 might be attributable to a primary salt effect and evidence has been presented to suggest that such an effect might not be negligible, but curvature is also seen in the data for the neutral Os^{II} complex (albeit less marked). It has been shown, in the previous paper,[6] that *N*-alkylation, far from further enhancing the reactivity of 5-chloro-1,10-phenanthroline with respect to methoxydechlorination, leads to compounds that do not release their chloride even after 30 min at 120 °C. This has been ascribed to the addition of methoxide to the carbon atom adjacent to the alkylated nitrogen (pseudo base formation) which serves to neutralise the charge on the nitrogen and reduces the extent of conjugation of the system. If co-ordination also enhances the ability of the substituted phenanthroline to form a pseudo base, one might expect a similar deactivation although it is unlikely that all three ligands in a tris species would be involved. However, each methoxide taken up would lower the charge of the complex by one unit and if, as we have suggested, the reactivity is sensitive to the overall charge on the complex, pseudo base formation would lead to a kinetic form of the type observed through the following process:

$$\begin{tikzcd} \text{substrate}^{2+} + \text{MeO}^- \arrow[r, "k_2^0"] \arrow[d, shift right, "+\text{MeO}^-"', "K"'] & \text{product} + \text{Cl}^- \\ \text{pseudo base}^+ + \text{MeO}^- \arrow[r, "k_2'"'] \arrow[u, shift right, "-\text{MeO}^-"'] & \text{product} + \text{Cl}^- \end{tikzcd}$$

which, if $k_2' \ll k_2^0$, should lead to the observed relationship, $k_{obs} = k_2^0[\text{MeO}^-](1 + K[\text{MeO}^-])^{-1}$. However, no changes to the ^{1}H n.m.r. spectrum of the type observed for 1-methyl-1,10-phenanthroline and 4,5-dihydro-3a,5a-diazoniapyrene were seen when methoxide ions were added to a solution of $[Ru(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$ and it is concluded that less than 10% of the co-ordinated ligand can be present in this form. The method is not sensitive enough to rule out the possibility that the observed curvature is due to the formation of an unreactive methoxide adduct but it is clear that such a species will not be an intermediate in the methoxydechlorination process.

EXPERIMENTAL

Preparations.—5-Chloro-1,10-phenanthroline was prepared by the method described in the previous paper.[6]

Tris(5-*chloro*-1,10-*phenanthroline*)*cobalt*(III) *perchlorate*. This was prepared by the method of Pfeiffer and Werdelmann.[17] 5-Chloro-1,10-phenanthroline (1.3 g) and chloropenta-amminecobalt(III) chloride (0.5 g) were dissolved in aqueous methanol (30—70 v/v; 150 cm^3) and the solution was refluxed for 6 h. A solution of sodium perchlorate (1 g) in water (10 cm^3) was added to the cooled reaction mixture to precipitate the yellow perchlorate which was filtered off, recrystallised several times from boiling water, and dried over P_2O_5.

Tris(5-*chloro*-1,10-*phenanthroline*)*nickel*(II) *perchlorate*. This was prepared by Pfeiffer's method.[18] A solution of $Ni(NO_3)_2\cdot6H_2O$ (0.6 g, AnalaR grade) in water (15 cm^3) was added to a solution of 5-chloro-1,10-phenanthroline (0.8 g) in methanol (15 cm^3) and the mixture was refluxed for 1 h. The pink solution was treated with solid sodium perchlorate and the pale pink precipitate was filtered off, recrystallised twice from hot water, and dried *in vacuo* over P_2O_5.

Tris(5-*chloro*-1,10-*phenanthroline*)*ruthenium*(II) *perchlorate*. This was prepared by the method of Dwyer.[19] $RuCl_3\cdot3H_2O$ (0.5 g) was dissolved in hot water (50 cm^3) containing one drop of 5M-hydrochloric acid and 5-chloro-1,10-phenanthroline (1.5 g) was added and the mixture shaken and heated to boiling for 10 min. Hypophosphorous acid (2 cm^3, 30%), which had been neutralised with 2M-sodium hydroxide solution, was then added and the mixture refluxed for 20 min. The deep orange-red solution was filtered and perchloric acid (10 cm^3, 60%) was slowly added to the hot filtrate. The orange-red precipitate was filtered off, dissolved in acetone, and the solution passed down a column of activated alumina. The desired product was eluted from the column with methanol, leaving a brownish green band at the top. The methanol was evaporated off and the residue recrystallised from hot water. The crystals were dried *in vacuo* over P_2O_5.

Tris(5-*chloro*-1,10-*phenanthroline*)*osmium*(II) *iodide*. This was prepared by Dwyer's method.[20] Ammonium hexabromo-osmate(III) (1.0 g) was dissolved in glycerol (20 cm^3) at 80—90 °C and 5-chloro-1,10-phenanthroline (1.3 g) was added. The temperature was raised to 270 °C and held there for 30 min. The mixture was cooled below 100 °C and poured into water (150 cm^3) that had been slightly acidified with hydrochloric acid. The solution was filtered, excess of potassium iodide was added, and the iodide that precipitated was filtered off and recrystallised from a small volume of hot water. The crystals were dried *in vacuo* over P_2O_5. The *perchlorate* was prepared by dissolving the iodide in hot water and adding a small volume of 10% aqueous sodium perchlorate solution. The precipitate was filtered off, washed with a little cold water, and recrystallised from hot water. The crystals were dried *in vacuo* over P_2O_5.

cis-*Dichlorobis*(5-*chloro*-1,10-*phenanthroline*)*osmium*(III) *chloride*. Potassium hexachloro-osmate(IV) (2 g) was suspended in anhydrous dimethylformamide (40 cm³) and 5-chloro-1,10-phenanthroline (2 g) was added and the reaction mixture refluxed for 2 h. The solution was filtered, ethanol (40 cm³) was added to the filtrate, and the complex precipitated by adding an excess of diethyl ether. It was filtered off, washed with ether, and dried at 40 °C.

Dichlorobis(5-*chloro*-1,10-*phenanthroline*)*osmium*(II). $[Os(5\text{-}Cl\text{-}phen)_2Cl_2]Cl$ (3 g) was dissolved in dimethylformamide (60 cm³) and methanol (30 cm³) and a dilute aqueous solution of sodium dithionite (600 cm³) was slowly added to the solution at room temperature. The product was cooled in an ice bath and the dark purple complex filtered off, washed with water, methanol, and diethyl ether, and dried at 40 °C. It was recrystallised from chloroform.

Acetylacetonatobis(5-*chloro*-1,10-*phenanthroline*)*osmium*(II) *chloride*. This was prepared by a modification of the method of Dwyer *et al.*[21] Acetylacetone (2 cm³) was added to a suspension of $[Os(5\text{-}Cl\text{-}phen)_2Cl_2]$ (2 g) in water (40 cm³) and ethanol (10 cm³) and the mixture was refluxed for 12 h in the presence of AnalaR calcium carbonate (2 g). The excess of ethanol was evaporated off, the solution filtered, and the filtrate extracted with chloroform (30 cm³). The extract was dried over anhydrous $MgSO_4$, evaporated to small volume, and the complex precipitated by adding diethyl ether. The dark purple solid was recrystallised from chloroform.

TABLE 4

Analytical data for the complexes

			C	H	N	Halogen	Metal
$[Co(5\text{-}Cl\text{-}phen)_3][ClO_4]_3$	Yellow	$C_{36}H_{21}Cl_6CoN_6O_{12}$				10.60 (10.62) [a]	5.88 (5.89)
$[Ni(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$	Pink	$C_{36}H_{21}Cl_5N_6NiO_8$	47.2 (4.80)	2.96 (2.35)	9.34 (9.32)	11.8 (11.8) [a]	6.54 (6.51)
$[Ru(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$	Red-orange	$C_{36}H_{21}Cl_5N_6O_8Ru$	44.6 (45.8)	3.07 (2.24)	8.80 (8.90)	11.30 (11.25) [a]	
$[Ir(5\text{-}Cl\text{-}phen)_2Cl_2]Cl$	Scarlet	$C_{24}H_{14}Cl_5IrN_4$	39.3 (39.6)	2.39 (1.94)	8.14 (7.69)	24.4 (24.3) [b] 4.9 (4.87) [c]	26.6 (26.4)
$[Os(5\text{-}Cl\text{-}phen)_3]I_2$		$C_{36}H_{21}Cl_3N_6I_2Os$			7.6 (7.7)	9.74 (9.78) [a] 23.2 (23.3) [d]	
$[Os(5\text{-}Cl\text{-}phen)_3][ClO_4]_2$		$C_{36}H_{21}Cl_5N_6O_8Os$				10.3 (10.3) [a]	
$[Os(5\text{-}Cl\text{-}phen)_2Cl_2]Cl$		$C_{24}H_{14}Cl_5N_4Os$				4.81 (4.89) [c]	
$[Os(5\text{-}Cl\text{-}phen)_2Cl_2]$	Dark purple	$C_{24}H_{14}Cl_4N_4Os$				20.3 (20.5) [b]	
$[Os(5\text{-}Cl\text{-}phen)_2acac]Cl$	Dark purple	$C_{29}H_{21}Cl_3N_4O_2Os$				14.0 (14.2) [b] 4.73 (4.73) [c]	
$[Os(5\text{-}Cl\text{-}phen)_2acac]ClO_4$	Dark purple	$C_{29}H_{21}Cl_3N_4O_6Os$				8.70 (8.67) [a]	
$[Os(5\text{-}Cl\text{-}phen)_2(C_2O_4)]$	Dark violet	$C_{26}H_{14}Cl_2N_4O_4Os$			7.89 (7.92)	10.04(10.01) [b]	

[a] Ligand chlorine. [b] Total chlorine. [c] Ionic chloride. [d] Iodide.

The *perchlorate* was obtained by adding sodium perchlorate to a solution of the chloride in water. The precipitate was filtered off, washed with water, and dried *in vacuo*.

Oxalatobis(5-*chloro*-1,10-*phenanthroline*)*osmium*(II). This was prepared by a modification of the method of Dwyer.[21] $[Os(5\text{-}Cl\text{-}phen)_2Cl_2]$ (0.6 g) was suspended in water (90 cm³) and ethanol (45 cm³) and refluxed with sodium oxalate (1.5 g). The starting material dissolved slowly and after 12 h the ethanol was evaporated off and the residual solution cooled in an ice bath. A dark purple material separated and was filtered off, washed with water, ethanol, and diethyl ether, recrystallised from chloroform, and dried *in vacuo*.

The microanalytical data for these complexes are collected in Table 4. In some cases the perchlorates gave poor and irreproducible combustion analysis results, presumably because of their explosive nature.

The Product of the Reaction between Tris(5-*chloro*-1,10-*phenanthroline*)*ruthenium*(II) *Perchlorate and Sodium Methoxide in Dimethyl Sulphoxide–Methanol Solution.*—At the end of the reaction, the solution was diluted with an equal volume of ethanol and the complex precipitated by adding diethyl ether. The precipitate was filtered off, washed with 0.1M-perchloric acid and water, and, because the perchlorate salt was unsuitable for combustion analysis, converted into the iodide. A solution of the perchlorate in aqueous dimethyl sulphoxide was passed down a column of strong cation exchange resin [Amberlite IR 120(H)] and the cation then eluted with concentrated hydrochloric acid. The effluent was evaporated to dryness and the residue dissolved in a small amount of water and treated with potassium iodide. The iodide precipitated and was filtered off, washed with water, and dried *in vacuo* (Found: C, 47.7; H, 4.2; I, 25.7. $C_{39}H_{30}I_2N_6O_3Ru$ requires C, 47.5; H, 3.1; I, 25.7%).

Solvents and Reagents.—Dimethyl sulphoxide and methanol were purified, dried, and stored as described in the previous paper.[6] Sodium methoxide solutions were prepared, standardised, and stored as before.

Kinetics.—The progress of the reaction was followed by titration of the released chloride in the way previously described.[6] Reaction solutions were prepared as before, except in the case of the faster reactions, where the solutions of the complex and the base were placed in separate parts of the apparatus and brought to the reaction temperature before mixing.

Colorimetric Estimation of Unco-ordinated 5-*Chloro*-1,10-*phenanthroline.*—An aliquot of reaction mixture was cooled to room temperature and extracted with portions of diethyl ether. The free ligand was extracted from the ether solution using 0.5M-sulphuric acid, ferrous sulphate solution was added and the mixture buffered to pH 5 to form the bright red Fe^{II} complex. The absorbance at the peak (512 nm) was measured and the concentration of ligand determined from the known molar extinction coefficient of $[Fe(5\text{-}Cl\text{-}phen)_3]^{2+}$ (11 300 dm³ mol⁻¹ cm⁻¹). Care must be taken to avoid adding too little or too much Fe^{II}. This method does not distinguish between 5-chloro- and 5-methoxy-1,10-phenanthroline.

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