# Autocatalytic Reduction of the *cis*-Bis(2,2′-bipyridyl)dichlororhodium-(III) Ion in Alkaline Aqueous Ethanol under a Hydrogen Atmosphere

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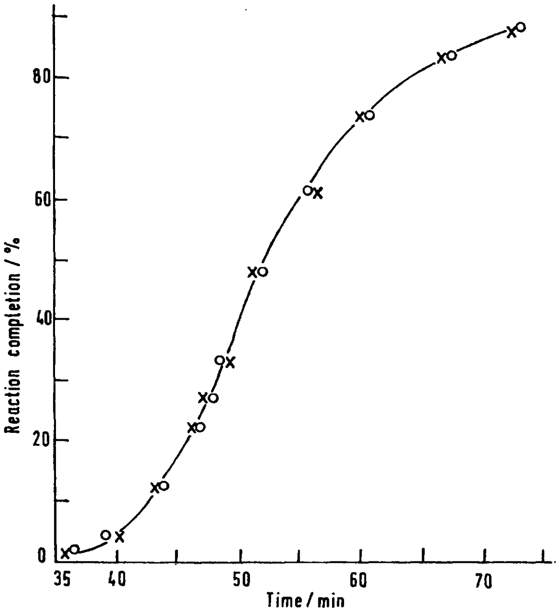
The ion *cis*-$[Rh(bipy)_2Cl_2]^+$ (bipy = 2,2′-bipyridyl) is reduced in alkaline aqueous ethanol under hydrogen to the known $[Rh(bipy)_2]^+$ ion. A detailed kinetic study of this reaction has been carried out and the rate equation governing the reaction is shown to be of the form $d[Rh^{I}]/dt = k[Rh^{III}]^2[Rh^{I}]$. The observed rate constant varies with hydroxide-ion concentration, but is independent of the concentration of added chloride ion. The variation of rate with temperature is also reported. A mechanism is postulated to account for the experimental results.

RHODIUM(I) complexes are known to catalyse the substitution reactions of rhodium(III) complexes; a summary of the relevant literature is given in the preceding paper. Here we describe detailed kinetic studies on the reduction of *cis*-$[Rh(bipy)_2Cl_2]^+$ to $[Rh(bipy)_2]^+$ (bipy = 2,2′-bipyridyl). In this system, the reaction is also catalysed by rhodium(I), but the overall reaction is now reduction rather than substitution. The ion *cis*-$[Rh(bipy)_2Cl_2]^+$ can be reduced to the lower oxidation state complex in a variety of ways: by the tetrahydroborate ion, sodium amalgam,[1] or by heating its solution in alkaline aqueous ethanol under hydrogen. This latter route has been studied in detail and the results are reported here.

## RESULTS

When a solution of the *cis*-bis(2,2′-bipyridyl)dichlororhodium(III) cation in alkaline aqueous ethanol is heated to 60 °C under a hydrogen atmosphere, hydrogen gas is consumed and the colour of the solution changes from pale yellow to violet. Manometric measurements of the volume of hydrogen consumed show that the ratio of rhodium(III) : hydrogen is 1 : 1. The spectrum of the violet solution produced in this reaction corresponds to that reported[1] for $Rh^{I}(bipy)_2$. When a concentrated solution of $[Rh(bipy)_2Cl_2](ClO_4),2H_2O$ is reduced under these conditions, and the violet solution then cooled in ice, violet crystals can be isolated; the latter are extremely air sensitive and appear to be identical with the rhodium(I) compound $[Rh(bipy)_2](ClO_4),2H_2O$.

Kinetic studies of this reduction reaction have been carried out both by measuring the volume of hydrogen consumed during the reaction, and by following changes in the optical density of the reaction solution at 557 nm. The rhodium(I) product exhibits a visible absorption at this wavelength ($\varepsilon$ = 3550 l mol$^{-1}$ cm$^{-1}$) which obeys Beer's law under the experimental conditions employed here. A concentration against time curve for a typical kinetic run is shown in the Figure, together with a computed fit. An induction period of variable duration is observed after the reagents have been mixed,[2] typically between 0·5 and 1 h. The extent of this induction period can be decreased by adding a small quantity of $[Rh(bipy)_2]^+$, by carrying out the experiment in a vessel which has not been rigorously cleaned after an earlier experiment, or by using a sample of $[Rh(bipy)_2Cl_2]^+$ prepared by the method of Gillard *et al.*[3] In the latter hydrazinium chloride is used as the catalytic reducing agent, and the product presumably contains some reducing agent or rhodium(I) as contaminant. The length of the induction period is increased if dissolved oxygen is present in the reaction solution. Oxygen also reoxidizes the final solution of rhodium(I) back to the rhodium(III) reactant.



Typical plot of the concentration of the rhodium(I) product against time. (×), Experimental points; (○), calculated fit based on equation (2)

When reaction commences, the rate profile is typical of an autocatalytic process. Analysis of the curve suggests that the major term in the rate law is as in equation (1).

$$d\,[Rh^{I}]/dt = k_{obs}\,[Rh^{III}]^2[Rh^{I}] \qquad (1)$$

The integrated form of this equation is (2), where $[Rh^{III}]_T$

$$k_{obs}\,t = \frac{1}{[Rh^{III}]_T^{\,2}}\left(\frac{[Rh^{III}]_T}{[Rh^{III}]_T - [Rh^{I}]_t} + \ln\frac{[Rh^{I}]_t}{[Rh^{III}]_T - [Rh^{I}]_t}\right) + \text{constant} \qquad (2)$$

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[1] B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nuclear Chem.*, 1961, **23**, 207.

[2] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1971, 1840.

[3] R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1965, 1951.

is the total rhodium concentration and $[\mathrm{Rh^I}]_t$ the concentration of the rhodium(I) product at time *t*. A least-squares computer program was used to calculate the best values for the observed rate constant and the integration constant (which includes the induction period). Good agreement up to 90% completion is found between observed values of $[\mathrm{Rh^I}]$ and those calculated using the computed constants. The sample curve in the Figure shows both observed and calculated values and typifies the degree of agreement found. The value for the overall rate constant, calculated from equation (2), remains constant within experimental error as the total rhodium concentration is varied between $2\cdot77 \times 10^{-4}$ and $1\cdot01 \times 10^{-3}$M, providing additional confirmation of the applicability of this equation.

The rate of reaction increases with temperature (Table 1) and a value of $20\cdot1 \pm 1\cdot6$ kcal mol$^{-1}$ is obtained for the parameter equivalent to an activation energy. The rate of reaction also varies with the hydroxide-ion concentration and the dependence found is expressed in equation (3).

TABLE 1

Variation of the observed rate constant with temperature. Initially, $[\mathrm{Rh^{III}}] = 5\cdot63 \times 10^{-4}$M, $[\mathrm{OH^-}] = 0\cdot194$M in ethanol (25%)–water under 1 atm hydrogen

| $t$/°C | $10^{-6}k_{\mathrm{obs}}$/l$^2$ mol$^{-2}$ min$^{-1}$ |
|---|---|
| 70·0 | 5·60 |
| 65·0 | 3·32 |
| 60·0 | 2·58 |
| 55·0 | 1·32 |
| 50·0 | 0·997 |
| 40·0 | 0·342 |

$$k_{\mathrm{obs}} = k'[\mathrm{OH^-}]/(k'' + [\mathrm{OH^-}]) \qquad (3)$$

Mean values of duplicate experiments are tabulated in Table 2, together with calculated values of *k*. The latter were obtained from equation (3) by setting $k' = 7\cdot0 \times 10^6$ l$^2$ mol$^{-2}$ min$^{-1}$ and $k'' = 0\cdot348$ mol l$^{-1}$.

TABLE 2

Variation of the observed rate constant with the hydroxide-ion concentration. Initially, $[\mathrm{Rh^{III}}] = 5\cdot63 \times 10^{-4}$M in ethanol (25%)–water under 1 atm hydrogen at 60 °C

| $[\mathrm{OH^-}]$/M | $10^{-5}k_{\mathrm{obs}}$/ l$^2$ mol$^{-2}$ min$^{-1}$ | $10^{-5}k_{\mathrm{calc}}$ $^a$/ l$^2$ mol$^{-2}$ min$^{-1}$ |
|---|---|---|
| 0·992 | 51·9 | 51·9 |
| 0·741 | 46·8 | 47·6 |
| 0·555 | 42·7 | 43·0 |
| 0·315 | 32·2 | 33·2 |
| 0·194 | 23·2 | 25·0 |
| 0·110 | 12·6 | 16·8 |
| 0·067 | 11·1 | 11·3 |
| 0·042 | 7·72 | 7·48 |
| 0·033 | 7·70 | 6·05 |
| 0·021 | 3·65 | 4·05 |

$^a$ $k_{\mathrm{calc}} = 7 \times 10^6[\mathrm{OH^-}]/(0\cdot348 + [\mathrm{OH^-}])$.

The addition of chloride ion, as analytical grade sodium chloride, has little effect on either the length of the induction period or the rate constant up to 1M (Table 3). At higher chloride-ion concentrations, purple precipitates, presumably $[\mathrm{Rh(bipy)_2}]\mathrm{Cl}$, appear. Similar precipitates begin to be visible at ionic strengths above 0·55M when sodium nitrate is added as an inert electrolyte; the narrow range of ionic strengths available precludes the use of nitrates as inert electrolytes. Unless the addition of sodium chloride produces two opposing effects which cancel out, the data of Table 3 show that the rate of reaction is independent of added chloride ion, and varies little with ionic strength above 0·315M. When the rhodium(III) reagent is used with chloride, perchlorate, or nitrate as the counter ion, the observed rate constant remains the same within experimental error. Thus, at concentrations of *ca.* $10^{-3}$M, these anions do not affect the rate of reaction.

TABLE 3

Effect of added chloride ion or 2,2′-bipyridyl on the observed rate constant at 60 °C, 1 atm hydrogen. Initially, $[\mathrm{Rh^{III}}] = 5\cdot63 \times 10^{-4}$M, $[\mathrm{OH^-}] = 0\cdot315$M in ethanol (25%)–water

| $[\mathrm{Cl^-}]$/M | $10^4$[bipy]/M | $10^{-6}k_{\mathrm{obs}}$/ l$^2$ mol$^{-2}$ min$^{-1}$ |
|---|---|---|
| 0 | 0 | 3·27 |
| 0·06 | 0 | 3·42 |
| 0·10 | 0 | 2·63 |
| 0·20 | 0 | 2·94 |
| 0·40 | 0 | 3·16 |
| 0·60 | 0 | 2·93 |
| 1·00 | 0 | 2·34 |
| 0 | 5·02 | 0·143 |
| 0 | 10·3 | 0·0764 |

The addition of free 2,2′-bipyridyl to the reaction mixture markedly slows down the rate of reaction and in order to obtain solutions in which the reaction proceeds to completion, the concentration of added ligand must be much less than a 20-fold excess relative to rhodium. Thus one cannot assume that the 2,2′-bipyridyl concentration remains essentially constant throughout the course of the reaction. Two results are cited in Table 3 for systems to which small quantities of 2,2′-bipyridyl have been added; in both cases the data were still governed by equation (2) (this point is significant to the subsequent discussion). The rate constant appears to vary with the reciprocal of the concentration of added 2,2′-bipyridyl. However, because of the low excess present, these data do not constitute absolute proof of this dependence.

All the reactions described so far were carried out in an ethanol (25%)–water mixture. We find, on varying the ethanol concentration, that the reaction requires the presence of ethanol; no reaction occurs in a purely aqueous medium, nor in a mixture of n-butanol and water. The rate of reaction decreases as the ethanol concentration increases in the range 1·43—7·63M (*i.e.* 8—45% v.v.), although the length of the induction period remains approximately constant. Above 7·63M the length of the induction period increases, and the reaction appears to follow a different course. At an ethanol concentration of 11·2M (66%), the initial rhodium(III) solution is a much more intense yellow-green colour than in more aqueous media, and an extremely oxygen-sensitive orange-brown solution is ultimately produced. In the range of ethanol concentrations from 1·43 to 7·63M, the observed rate constant appears to depend on the ethanol concentration to the power $-\frac{1}{2}$ (Table 4).

Some kinetic experiments were also carried out in which the 2,2′-bipyridyl ligands were replaced by substituted bipyridyl or 1,10-phenanthroline molecules; in all cases it was observed that the change of ligand caused a diminution in the observed rate constant (Table 5).

The final experiments to be described are those in which the reaction was followed not by spectrophotometric techniques, as above, but by following the uptake of hydrogen manometrically. As in the former, the physical conditions used involved vigorously shaking the reaction solution

TABLE 4

Variation of the observed rate constant with ethanol concentration. Initially, $[\mathrm{Rh^{III}}] = 5{\cdot}63 \times 10^{-4}$M, $[\mathrm{OH^-}] = 0{\cdot}187$M under 1 atm hydrogen at 55·0 °C

| [EtOH]/M | $10^{-6}k_{\mathrm{obs}}$/ l² mol⁻² min⁻¹ |
|---|---|
| 1·43 | 2·52 |
| 2·56 | 1·70 |
| 3·42 | 1·52 |
| 4·28 | 1·30 |
| 7·64 | 0·93 |

TABLE 5

Observed rate constants for the complexes *cis*-$[\mathrm{RhL_2Cl_2}]^+$ in ethanol (25%)–water under 1 atm hydrogen; various initial concentrations of the rhodium complexes

| Ligand [a] | $t$/°C | $[\mathrm{OH^-}]$/M | $10^{-6}k_{\mathrm{obs}}$/ l² mol⁻² min⁻¹ |
|---|---|---|---|
| 2,2′-bipy | 60 | 0·194 | 2·40 |
| 4,4′-$\mathrm{Cl_2}$-bipy | 70 | 0·194 | 0·100 |
| 4,4′-$\mathrm{Me_2}$-bipy | 60 | 0·194 | 0·416 |
| 5,5′-$\mathrm{Me_2}$-bipy | 60 | 0·194 | 0·616 |
| 1,10-phen | 60 | 0·315 | 1·37 |
| 1,10-phen | 70 | 0·315 | 1·50 |
| 5-$\mathrm{NO_2}$-phen | 70 | 0·315 | 0·430 |
| 3,4,7,8-$\mathrm{Me_4}$-phen | 70 | 0·315 | 0·0390 |

[a] The nomenclature used is such that 4,4′-$\mathrm{Cl_2}$-bipy represents 4,4′-dichloro-2,2′-bipyridyl.

under hydrogen gas at a constant pressure. It should be noted that the agitation produced by the use of a magnetically propelled bead was insufficient to maintain a constant concentration of dissolved hydrogen. The rate-determining step is the rate of solution of hydrogen. By using solutions which take up the minimum measurable volume of gas, *i.e.* $1{\cdot}3 \times 10^{-3}$—$4{\cdot}3 \times 10^{-3}$M solutions of the rhodium(III) reagent, and by shaking the reaction vessel vigorously, this problem can be overcome.

Under these conditions, an induction period is still observed, unlike the reaction between rhodium(III) and carbon monoxide.[4] The rate of consumption of hydrogen obeys equation (1) after this period, with the modification that 'hydrogen consumed' replaces 'rhodium(I) produced'. Unfortunately the vigorous vibration of the equipment and the small volume changes occurring produce large errors in the experimental results. Duplicate experiments resulted in calculated rate constants which differed by as much as 50%. However, these inaccurate values do agree, within their experimental error, with the values determined spectrophotometrically. The magnitude of the errors in the spectrophotometrically studied experiments can be seen from a comparison of the data quoted in Tables 1, 2, and 5. These data are distinct, having been obtained at different times using different reagent samples and solutions, and show a standard deviation of 4%.

In summary, the reaction studied is described by equation (4), where $k_{\mathrm{a}}$ and $k_{\mathrm{b}}$ are constants at a given temperature. The dependence on [bipy] has not been conclusively proven (see above).

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Rh}]^{\mathrm{I}} = \frac{k_{\mathrm{a}}[\mathrm{Rh^{III}}]^2[\mathrm{Rh^I}][\mathrm{OH^-}][\mathrm{Cl^-}]^0}{[\mathrm{bipy}][\mathrm{EtOH}]^{\frac{1}{2}}(k_{\mathrm{b}} + [\mathrm{OH^-}])} \tag{4}$$

Investigation, using ¹H n.m.r., e.s.r., and i.r. spectroscopy, of samples obtained by quenching half-reacted reaction solutions provided no evidence of metal hydrides or paramagnetic species. Such species must either be absent, or present only at low concentrations. Finally, when a $4{\cdot}25 \times 10^{-3}$M solution of the rhodium(III) complex in ethanol (25%)–water containing 0·309M-hydroxide is warmed to 60 °C under a nitrogen atmosphere, the rhodium(I) product is formed very slowly. Approximately 6 h are required for 50% completion. Thus there is a slow reaction involving ethanol which could produce rhodium(I) during the observed induction period.

## DISCUSSION

The reduction of *cis*-$[\mathrm{Rh(bipy)_2Cl_2}]^+$ to $[\mathrm{Rh(bipy)_2}]^+$, under the present experimental conditions, involves two distinct stages. First there is an induction period during which a slow build up of the rhodium(I) product occurs; this is followed by a faster autocatalytic reduction involving hydrogen. The observation that slow reduction to $[\mathrm{Rh(bipy)_2}]^+$ occurs under a nitrogen atmosphere shows that alkaline ethanol is capable of reducing the rhodium(III) complex, and therefore initiating the faster autocatalytic process during the induction period. The extent of this period can be reduced by introducing a small amount of product.

The effect of added 2,2′-bipyridyl on the slow reoxidation of the rhodium(I) complex in ethanol (25%)–water has been interpreted [1] as indicating that dissociation of the bis-rhodium(I) complex occurs. Also, when a sample of *cis*-$[\mathrm{Rh(bipy)_2Cl_2}]^+$ is reduced by sodium tetrahydroborate in methanol, and triphenylphosphine is then added, $[\mathrm{Rh(bipy)(PPh_3)_2H_2}](\mathrm{ClO_4})$ can be isolated.[5] We therefore believe that the retardation, observed by us, when 2,2′-bipyridyl is added to a reaction solution, is due to suppression of a dissociation equilibrium. The rate law is not altered by this addition, while the observed rate constant seems to be inversely proportional to the concentration of added ligand. These observations are consistent with the proposed reaction scheme, equations (5)—(9), if the steady-state hypothesis holds for all monobipyridyl intermediates, and the 2,2′-bipyridyl concentration therefore remains constant.

$$\mathrm{H_2(solv)} + [\mathrm{RhL_2}]^+ \overset{K_1}{\rightleftharpoons} \underset{\mathrm{A}}{[\mathrm{H_2RhL}]} + \mathrm{L} \tag{5}$$

$$\underset{\mathrm{A}}{[\mathrm{H_2RhL}]^+} + [\mathrm{RhL_2Cl_2}]^+ \overset{K_2}{\rightleftharpoons} \underset{\mathrm{B}}{[\mathrm{H_2LRhClRhL_2Cl}]^{2+}} \tag{6}$$

$$\underset{\mathrm{B}}{[\mathrm{H_2LRhClRhL_2Cl}]^{2+}} + [\mathrm{RhL_2Cl_2}]^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\mathrm{C}}{[\mathrm{ClL_2RhCl(RhLH_2)ClRhL_2Cl}]^{3+}} \tag{7}$$

$$\underset{\mathrm{C}}{[\mathrm{ClL_2RhCl(RhLH_2)ClRhL_2Cl}]^{3+}} + \mathrm{OH^-} \xrightarrow{k_4} \underset{\mathrm{D}}{[\mathrm{ClL_2RhCl(RhLH)ClRhL_2Cl}]^{2+}} + \mathrm{H_2O} \tag{8}$$

$$\underset{\mathrm{D}}{[\mathrm{ClL_2RhCl(RhLH)ClRhL_2Cl}]^{2+}} + \mathrm{OH^-} \xrightarrow{\text{fast}} [\mathrm{RhL_2Cl_2}]^+ + [\mathrm{RhL_2}]^+ + [\mathrm{RhL}]^+ + \mathrm{H_2O} + 2\mathrm{Cl^-} \tag{9}$$

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[4] B. R. James and G. L. Rempel, *J. Chem. Soc.* (*A*), 1969, 78.

[5] Personal communication from I. I. Bhayat and W. R. McWhinnie.

The replacement[2] of X by Z in *trans*-$[Rh(py)_4X_2]^+$ ($X = Cl^-$ or $Br^-$; $Z = Br^-$ or $Cl^-$) is catalysed by rhodium(I), while the rate of reaction is independent of the concentration of Z. We believe that the absence of chloride-ion dependence in the autocatalytic reaction studied here is due to a similar process, as shown in equation (6), namely the formation of a chloro-bridged dimer by the interaction of a rhodium(I) with a rhodium(III) ion.

Hydrogen is consumed during the rapid autocatalytic reaction, at the same rate as rhodium(I) is produced. The most likely mode of uptake of hydrogen is that of an oxidative addition to the rhodium(I) complex. Any such hydrides must be in low concentrations since we have been unable to detect their presence. The variation of the rate of reaction with hydroxide-ion concentration is consistent with its involvement in a process which may be generalized as in (10), where A and B represent

$$\begin{gathered} A \rightleftharpoons B \\ B + OH^- \longrightarrow \text{products} \end{gathered} \qquad (10)$$

intermediate species, and the steady-state hypothesis applies to B. Equations (7) and (8) in the postulated reaction scheme are of this form, while equation (8) essentially represents[2] the process (11).

$$Rh^{III}\text{-}H + OH^- \longrightarrow Rh^I + H_2O \qquad (11)$$

The overall rate law for the reduction of *cis*-$[Rh(bipy)_2Cl_2]^+$ exhibits a second-order dependence on the concentration of the rhodium(III) complex. Such a dependence could be due to an inner- or an outer-sphere reaction between the reactant and an intermediate dimer. There is no evidence available which could be used to distinguish between these possibilities. We prefer to postulate the formation of a trimer.

Although we observe a systematic relationship between the observed rate constant and the concentration of ethanol in the reaction medium, we do not believe that an interpretation of this dependence is justified. When the ethanol concentration is altered, several parameters which could affect the rate of reaction are altered. For example the structure of the solvent medium, the solubility of hydrogen, and the solvation of reactants will vary. Ethanol is certainly required for the overall reaction to occur, as shown in the Results section.

Our experiments lead us to suggest that the sequence of reactions (5)—(9) represents the overall reaction studied here. In this scheme the symbol L is used to represent 2,2′-bipyridyl. Although molecules of water or ethanol may well behave as ligands, their presence is not shown. The application of the steady-state hypothesis to the intermediates labelled A—D, means that the concentration of L remains constant and the overall rate law is that of equation (12):

$$\frac{d}{dt}[Rh^I] = \frac{K_1K_2k_3k_4[Rh^{III}]^2[Rh^I][OH^-][H_2(solv)]}{[bipy](k_{-3} + k_4[OH^-])} \qquad (12)$$

This equation is of the same form as equation (4); the symbol $k''$ in equation (3) is equal to the ratio $k_{-3} : k_4$.

When complexes are studied which contain substituted bipyridyl, phenanthroline, or substituted phenanthroline molecules as ligands rather than unsubstituted 2,2′-bipyridyl, the rate of reaction decreases as shown in Table 5. The changes cannot be explained purely in terms of electronic effects on either rhodium(III) or rhodium(I). The more bulky a substituent on the ligands, the slower the rate becomes. Therefore it seems that the main effect of ligand changes on the rate of reaction is due to steric effects. These could be effects within the dimeric or trimeric intermediates, or changes in the degree of solvation of species on going from one ligand to another.

## EXPERIMENTAL

Kinetic studies were carried out in one of two ways: spectrophotometrically using the technique described previously,[6] or by measuring the volume changes in a volume of gas above the reaction solution. In the latter, two identical vessels were used which had outer jackets through which thermostat water was circulated. The vessels were mounted in a laboratory shaker to allow agitation of the solution to be achieved. In one vessel was placed the reaction solution, and in the other an identical mixture from which the rhodium(III) complex had been omitted. The reaction vessel and the blank were then connected by side arms of equal volume to the two arms of a manometer containing butyl phthalate. The volume of gas above the reaction solution was then adjusted, using a mercury-filled reservoir and manometer, to maintain an equal pressure in both sides of the equipment. Thorough flushing was always undertaken to ensure the absence of oxygen from the system.

cis-*Bis*(2,2′-*bipyridyl*)*dichlororhodium*(III) *Nitrate Dihydrate*.—Samples of this complex, and related complexes with other counter ions or substituted bipyridyl or phenanthroline ligands, were prepared by literature methods.[3,7,8] The nitrate salts, which are very soluble, were precipitated from solution by adding sodium nitrate (AnalaR) to their solutions. In some cases they crystallised out with incorporated sodium nitrate. This phenomenon is seen in Table 6 where analytical data are collected together.

*Bis*-(2,2′-*bipyridyl*)*rhodium*(I) *Perchlorate Trihydrate*.—A method for the preparation of this complex is available in the literature. A sample was also prepared under essentially the same conditions as those under which kinetic results were obtained in order to demonstrate that the same product was obtained. In this method 0·7M-sodium hydroxide solution (20 cm$^3$) was added to aqueous ethanol (50%, 20 cm$^3$) and the mixture thoroughly flushed with hydrogen. Solid *cis*-$[Rh(bipy)_2Cl_2](ClO_4),2H_2O$ (0·9 g) was then added and the mixture stirred and heated almost to boiling. When the colour change appeared to be complete, the vessel was cooled in an ice bath, whereupon violet crystals were formed; the nitrate and chloride salts crystallise less readily. The product was filtered off under a

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[6] J. D. Miller and F. D. Oliver, preceding paper.

[7] G. C. Kulasingam, W. R. McWhinnie, and J. D. Miller, *J. Chem. Soc.* (*A*), 1969, 521.

[8] E. D. McKenzie and R. A. Plowman, *J. Inorg. Nuclear Chem.* 1970, **32**, 199.

TABLE 6

Analytical data for compounds prepared and described herein

| | Observed % | | | | | | Calculated % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | C | H | Cl | N | Na | Rh | C | H | Cl | N | Na | Rh |
| $[Rh(bipy)_2Cl_2](NO_3),2H_2O$ | 41·1 | 3·5 | 11·8 | 12·0 | | 17·6 | 41·8 | 3·0 | 12·1 | 12·1 | 0 | 17·6 |
| $[Rh(bipy)_2Cl_2]Cl,2H_2O$ | 41·8 | 4·5 | | 9·9 | | 18·3 | 43·1 | 3·6 | 19·1 | 10·0 | 0 | 18·4 |
| $[Rh(bipy)_2Cl_2](ClO_4),2H_2O$ | 39·1 | 2·9 | | 9·4 | | 16·5 | 38·6 | 3·2 | 17·1 | 9·0 | 0 | 16·6 |
| $[Rh(4,4'\text{-}Cl_2\text{-}bipy)_2Cl_2](NO_3),2{\cdot}5NaNO_3$ | 27·7 | 1·6 | | 10·3 | 6·4 | 11·2 | 26·7 | 1·4 | 23·6 | 10·1 | 6·4 | 11·4 |
| $[Rh(4,4'\text{-}Me_2\text{-}bipy)_2Cl_2](NO_3),2H_2O$ | 44·7 | 4·0 | | 11·2 | | 16·2 | 45·0 | 4·4 | 11·1 | 10·9 | 0 | 16·1 |
| $[Rh(5,5'\text{-}Me_2\text{-}bipy)_2Cl_2](NO_3),2H_2O$ | 43·4 | 3·7 | | 11·1 | | 15·9 | 45·0 | 4·4 | 11·1 | 10·9 | 0 | 16·1 |
| $[Rh(phen)_2Cl_2](NO_3),1{\cdot}5NaNO_3$ | 39·3 | 2·5 | | 12·0 | 4·8 | 14·0 | 39·8 | 2·2 | 9·8 | 12·6 | 4·8 | 14·2 |
| $[Rh(5\text{-}NO_2\text{-}phen)_2Cl_2](NO_3),3{\cdot}5NaNO_3,5H_2O$ | 26·5 | 2·0 | | 13·8 | 7·3 | 9·8 | 26·8 | 2·3 | 6·5 | 13·7 | 7·5 | 9·6 |
| $[Rh(3,4,7,8\text{-}Me_4\text{-}phen)_2Cl_2](NO_3),0{\cdot}5NaNO_3,3H_2O$ | 47·0 | 4·2 | | 9·7 | 1·6 | 12·9 | 47·8 | 4·8 | 8·8 | 9·6 | 1·4 | 12·8 |
| $[Rh(bipy)_2](ClO_4),5H_2O$ | 38·8 | 3·8 | 5·9 | 9·3 | | 17·5 | 39·8 | 4·3 | 5·9 | 9·3 | 0 | 17·0 |

hydrogen atmosphere, washed with hydrogen-saturated water, and dried *in vacuo* overnight. The solid is extremely oxygen-sensitive, rapidly becoming grey on exposure to air.

Rhodium trichloride (40·6% rhodium) was provided by Johnson, Matthey Ltd. and samples of substituted bipyridyls by I.C.I. (Dyestuffs Division). All other reagents used were of analytical grade. The rhodium content of samples was estimated spectrophotometrically by first destroying the organic ligand with concentrated sulphuric acid and roasting, treating the resultant solution with concentrated hydrochloric acid and tin(II) chloride (18%, AnalaR) solution, and then measuring the optical density at 457 nm. A sample of rhodium trichloride of known composition was used as calibrant. An E.E.L. flame photometer Mark II was used to determine the sodium content. All other analytical data were provided by the microanalytical department of the University of Aston in Birmingham.

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