# Mechanism of Oxidative Dehydrogenation of Alcohols co-ordinated to Ruthenium†

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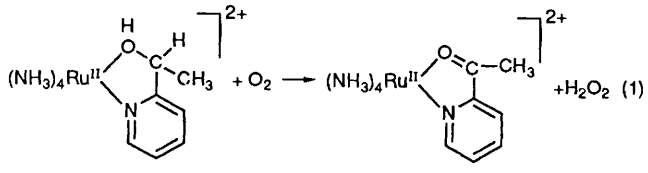
The oxidative dehydrogenation of the complexes $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$, $[Ru(bipy)_2(NC_5H_4CD_2OH)]^{2+}$ and $[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}]^{2+}$ to the corresponding carbonyl species [bipy = 2,2'-bipyridine; $NC_5H_4CH_2OH$ = 2-(hydroxymethyl)pyridine; $NC_5H_4CD_2OH$ = 2-(dideuteriohydroxymethyl)pyridine; $NC_5H_4CH(CH_3)OH$ = 2-(1-hydroxyethyl)pyridine] has been studied in aqueous solution by kinetic and electrochemical techniques. The mechanistic scheme was found to involve the intermediacy of a ruthenium(IV)–alkoxide species, formed by disproportionaton of the ruthenium(III) complex produced in the initial step of the oxidation process. The rate-determining removal of the proton from the α-carbon atom of the chelate ring is general-base catalysed.

The oxidation of alcohols is a reaction of considerable importance. By way of two significant but disparate examples, the process is fundamental to the action of a number of dehydrogenases in living cells and to the operation of alcohol fuel cells.

Although the catalytic oxidation of alcohols by transition metals is known in a few cases, the intimate mechanistic details of the oxidative dehydrogenation reactions themselves have rarely been elucidated. For example, Gagne and Marks[1] reported the catalysis of the autoxidation and electrochemical oxidation of alcohols by [1,3-bis(4-methyl-2-pyridyl)isoindoline]trichlororuthenium(III). The essential feature of the proposed reaction path was that the catalyst underwent substitution at the metal centre by the substrate alcohol, whose oxidation took place while it was co-ordinated. By analogy with a previous stoichiometric study by Tovrog *et al.*[2] of the reaction (1), the details of the ligand oxidation process were assumed to

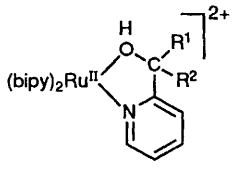



occur *via* a ruthenium(IV) intermediate, formed under basic conditions by disproportionation of the ruthenium(III) complex.

As part of a continuing general mechanistic study of ligand oxidation reactions,[3,4] we had undertaken an investigation of the oxidation [equation (2)] of a series of related alcohols co-ordinated to ruthenium,‡ **1a**–**1c**, reported here in detail, which verifies the intermediacy of the high-oxidation-state transient and elucidates details of the ligand dehydrogenation process.

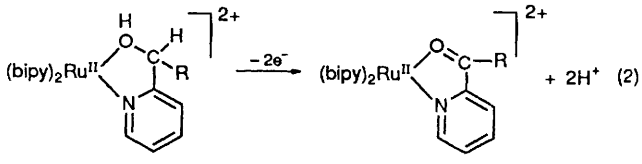
## Results and Discussion

*Synthesis and Characterization of Alcohol Complexes and their Oxidation Products.*—Alcohol complexes of the general




| | $R^1$ | $R^2$ |
|---|---|---|
| **1a** | H | H |
| **1b** | D | D |
| **1c** | H | $CH_3$ |
| **1d** | $CH_3$ | $CH_3$ |

bipy = 2, 2'-bipyridine




formulation **1** were synthesized in an analogous manner to the corresponding amine complexes[3,4] by reaction of the appropriate ligand with $[Ru(bipy)_2Cl_2]$ in acidic§ aqueous methanol. The $^1H$ NMR spectral data confirm the bidentate ligating mode of these ligands. For example, the spectrum of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ **1a** in $(CD_3)_2SO$ reveals an AB quartet centred at δ 5.18 which is attributed to the methylene protons rendered inequivalent because of the restricted conformational flexibility of the chelate ring. There is also a singlet at δ 9.53, attributed to the proton of the co-ordinated alcohol group and which exchanges on the addition of $D_2O$.

Synthesis of the species $[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}]^{2+}$ **1c** realized the two diastereoisomeric pairs in approximately equimolar amounts. They were partially separated by fractional crystallization (iodide salt), and each diastereoisomer could be enriched to *ca.* 80% isomeric purity by repeated crystallizations (monitored by the methyl doublet $^1H$ NMR resonances). Attempts to separate the two diastereoisomeric pairs chromatographically in the same manner as for the amine analogues[4] were unsuccessful, due to gradual oxidation of the complex under the conditions (pH 3; 4 °C) and the timescale (*ca.* 2 weeks) of the separation.

Comparative $^1H$ NMR nuclear Overhauser effect (NOE) difference studies of the Λ(*S*)/Δ(*R*)-$[Ru(bipy)_2\{NC_5H_4CH$-

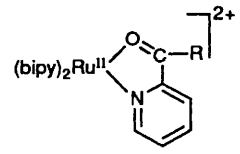
† *Non-SI unit employed:* mmHg ≈ 133 Pa.

‡ Presented at the 187th National American Chemical Society Meeting, St. Louis, MO, April 1984, Abstract INOR 191.

§ The alcohol complexes are susceptible to aerial oxidation at higher pH.

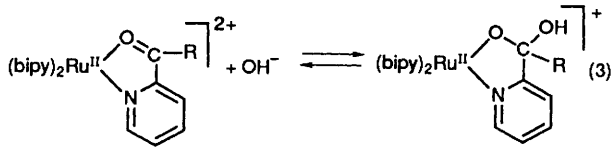
$(CH_3)NH_2\}]^{2+}$ (for which a crystal structure has been determined)[4] and $\Lambda(R)/\Delta(S)$-$[Ru(bipy)_2\{NC_5H_4CH(CH_3)NH_2\}]^{2+}$ diastereoisomers, and the diastereoisomers **A** and **B** of the corresponding alcohol species $[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}]^{2+}$ have allowed assignment of the stereochemistry of the latter. By observation of the enhancements resulting from the selective irradiation of the methyl protons, and separately the methine protons, in each case the higher-field methyl resonance may be associated with an equatorial orientation of the methyl group relative to the mean plane of the chelate ring.* The configuration of the less-soluble diastereoisomer of $[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}]^{2+}$ **A** may therefore be assigned as $\Lambda(S)/\Delta(R)$. The major difference between the analogous amine and alcohol species is that in $\Lambda(R)/\Delta(S)$-$[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}]^{2+}$ **B** the methyl group is more distinctly axial (and the methine proton more distinctly equatorial) compared with the amine counterpart. This observation may explain the greater difference in chemical shifts for the methyl groups in the alcohol (δ 1.25 and 1.73) compared with the amine (δ 1.51 and 1.68) diastereoisomers, although this effect may also be electronic in origin.

The $pK_a$ of the alcohol proton in $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ **1a** was determined to be 7.2 ± 0.2 at 25 °C ($I$ = 0.1 mol $dm^{-3}$, $LiNO_3$). For the monomethyl-substituted complex **1c** a determination of the $pK_a$ of the diastereoisomeric mixture under the same conditions gave one value (7.6 ± 0.2). Since the method is sufficiently sensitive to detect the presence of two different acidic species if their $pK_a$ values differ by 0.5, in the present case the two acidities must be similar. For the dimethyl-substituted species **1d** the $pK_a$ = 8.29 ± 0.01 under the same conditions.



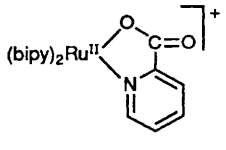

R
**2a** H
**2b** $CH_3$

The corresponding aldehyde **2a** and ketone **2b** complexes were synthesized by reaction of the appropriate ligand with $[Ru(bipy)_2(O_3SCF_3)_2]$ in dichloromethane under mild conditions. Under basic conditions these complexes were observed to undergo hydrate formation [equation (3)] in an analogous way to the reactions of the complexes of similar ligands with the $[Ru(NH_3)_4]^{2+}$ moiety.[5] The $^1H$ NMR spectrum of $[Ru(bipy)_2(NC_5H_4CHO)]^{2+}$ in $(CD_3)_2SO$ shows a singlet resonance at δ 10.38 which shifts to δ 5.99 on the addition of water due to hydrate formation of this type. The equilibrium constant for equation (3) (R = H) in aqueous solution was determined by a spectroscopic method similar to that reported by Alvarez *et al.*[5]



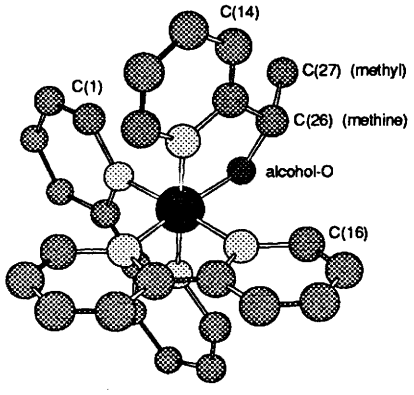

It was found that the concentrations of the aldehyde and hydrate species were equal at pH 7.95 ($I$ = 1.00 mol $dm^{-3}$, NaCl; 25 °C) so that $K = 6.03 \times 10^5$ $dm^3$ $mol^{-1}$, assuming $pK_w$ = 13.73 under these conditions.[6] This determination compares with values for $pK_{hyd}$ (= pH where [aldehyde] = [hydrate]) of 6.5 and 6.7 obtained by Blaho and Goldsby[7] for the same system using electrochemical and spectroscopic methods respectively, although the temperature and ionic strength of the medium were not disclosed by these authors. A value of $K$ = 140 ± 10 $dm^3$ $mol^{-1}$ was obtained for $[Ru(NH_3)_4(NC_5H_4CHO)]^{2+}$ under the same conditions as in the present study.[5] Accordingly, substitution of two bipy ligands for the four ammine ligands results in considerable activation of the co-ordinated aldehyde to nucleophilic attack by $OH^-$. Alvarez *et al.*[5] proposed that the stability of the aldehyde form in $[Ru(NH_3)_4(NC_5H_4CHO)]^{2+}$ resulted from π-back donation from the metal into the conjugated ligand system. In $[Ru(bipy)_2(NC_5H_4CHO)]^{2+}$ the extent of this back bonding from the metal to the conjugated system would be reduced due to metal-to-bipy back bonding present in the complex, resulting in decreased stability of the aldehyde form.

The complex $[Ru(bipy)_2(NC_5H_4CO_2)]^+$ **3** was prepared by reaction of pyridine-2-carboxylic acid with $[Ru(bipy)_2Cl_2]$ in an analogous manner to the syntheses of the alcohol complexes. For $[Ru(NH_3)_4(NC_5H_4CO_2H)]^{2+}$, $pK_a$ = 0.7,[5] substitution of the ammine ligands by bipyridine would be expected to increase that acidity since back bonding from $Ru^{II}$ to bipy enhances the Lewis acidity of the metal centre. Accordingly, $[Ru(bipy)_2(NC_5H_4CO_2)]^+$ would not be expected to be protonated, even under strongly acidic conditions.




**3**

The visible spectra in 0.1 mol $dm^{-3}$ HCl of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$, $[Ru(bipy)_2(NC_5H_4CHO)]^{2+}$ and its hydrate, and of $[Ru(bipy)_2(NC_5H_4CO_2)]^+$ are shown in Fig. 1.




* The numbering scheme used in Fig. 2 of ref. 4 for the molecular structure of $\Lambda(S)/\Delta(R)$-$[Ru(bipy)_2\{NC_5H_4CH(CH_3)NH_2\}]^{2+}$ is adopted for the following. Irradiation of the $CH_3$ group resulted in enhancement (3%) of the proton attached to C(14) in the pyridine ring of $NC_5H_4CH(CH_3)NH_2$, the methine proton (2%), the proton attached to C(1) in the neighbouring bipy ring (1%) and one NH proton (1%). Irradiation of the methine proton resulted in enhancement (4%) of signals from the proton attached to C(16) in a neighbouring bipy ring, the proton attached to C(14) (2%), the methyl protons (9%), with an additional minor enhancement of the signal from the other NH proton. For the $\Lambda(R)/\Delta(S)$ diastereoisomer, irradiation of the methyl group resulted in enhancements of the proton signal on C(14) (3%), the methine proton (3%) and one NH proton (1%). Irradiation of the methine proton resulted in enhancements of the proton on C(1) (6%), the proton attached to C(14) (2%), and the other NH proton (2%). For the alcohol complexes the description of the NOE results for the $\Lambda(S)/\Delta(R)$-$[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}]^{2+}$ diastereoisomer is essentially identical to that for the amine analogue, except for enhancements of the OH signal on irradiation of both the methyl (1%) and methine (3%) protons. However, for the $\Lambda(R)/\Delta(S)$ diastereoisomer there is a significant additional enhancement (2%) of the proton attached to C(16) when the methyl group is irradiated, and less enhancement of the signals of the protons attached to C(1) (3%) and C(14) (1%) when the methine proton is irradiated: from a study of molecular models, these observations can be rationalized in terms of a significantly greater axial orientation of the methyl group (and equatorial orientation of the methine hydrogen) relative to the mean plane of the chelate ring compared with the amine analogue.

**Table 1** Electrochemical and spectral (electronic, NMR) data on ruthenium complexes reported in this study

| Complex | $E_{\frac{1}{2}}$/V *vs.* SSCE | $\lambda_{max}$[a]/nm ($10^{-3}$ ε/dm$^3$ mol$^{-1}$ cm$^{-1}$) | $^1$H NMR[b] (non-aromatic protons) |
|---|---|---|---|
| **1a** ($R^1 = R^2 = H$) | 0.62[c] | 464 (8.5), 332 (9.0) | 9.53 (s, OH), 5.18 (q, $CH_2$) |
| **1b** ($R^1 = R^2 = D$) | 0.62[c] | 465 (8.7), 334 (9.1) | 9.53 (s, OH) |
| **1c** ($R^1 = H$, $R^2 = CH_3$) | | | |
| isomer **A** | 0.625[c] | 467 (8.4), 333 (9.0) | 1.25 (d, $CH_3$), 5.78 (q, CH), 9.39 (s, OH) |
| isomer **B** | 0.615[c] | 466 (8.5), 333 (9.0) | 1.73 (d, $CH_3$), 5.06 (q, CH), 9.60 (s, OH)[d] |
| **1d** ($R^1 = R^2 = CH_3$) | 0.50[c] | 466 (8.5), 333 (9.0) | 1.22 (s, $CH_3$), 1.84 (s, $CH_3$) |
| **2a** (R = H) | 1.28[e] | 433 (8.4) | 10.38 (br, CHO) |
| **2b** (R = $CH_3$) | 1.24[e] | 434 (8.5) | 3.66 (s, $CH_3$) |
| **2c** (R = D) | 1.28[e] | 433 (8.4) | |
| **3** | 0.85[c] | 469 (8.5) | |

[a] In 0.1 mol dm$^{-3}$ HCl solution. [b] In $(CD_3)_2SO$ solvent; chemical shift values quoted relative to $SiMe_4$ (internal). [c] In 0.1 mol dm$^{-3}$ HCl solution; platinum working electrode. [d] There is a very small coupling between the methine and the alcohol protons for this diastereoisomer only. [e] In propylene carbonate–0.2 mol dm$^{-3}$ $NEt_4ClO_4$; glassy carbon working electrode.

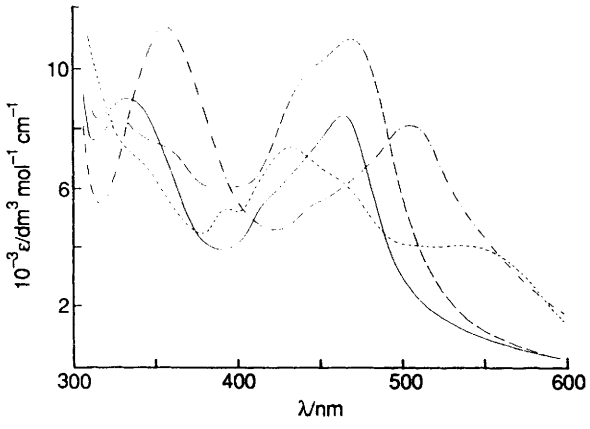



**Fig. 1** Electronic spectra (in 0.1 mol dm$^{-3}$ HCl) of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ (——), $[Ru(bipy)_2(NC_5H_4CHO)]^{2+}$ (· · · ·), $[Ru(bipy)_2\{NC_5H_4CH(O^-)OH\}]^+$ (— · — · —), $[Ru(bipy)_2(NC_5H_4CO_2)]^+$ (– – – –)

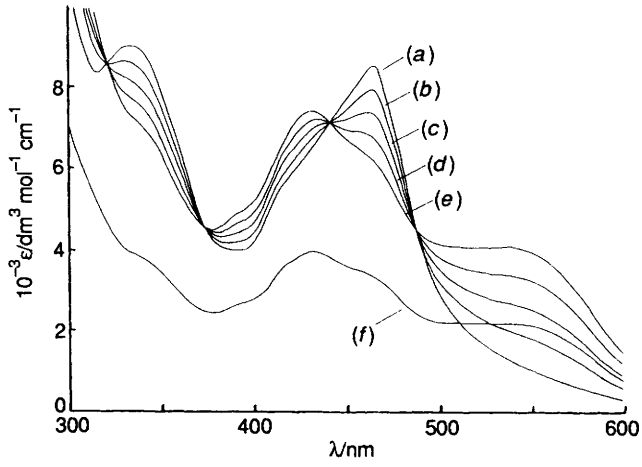



**Fig. 2** Spectrocoulometric oxidation of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ in 0.1 mol dm$^{-3}$ $CF_3SO_3H$–0.9 mol dm$^{-3}$ NaCl ($E$ = 0.65 V *vs.* SSCE, platinum working electrode). Coulometric $n$ electrons per $Ru^{II}$: (*a*) 0, (*b*) 0.5, (*c*) 1.0, (*d*) 1.5, (*e*) 2.0 and (*f*) 2.5

A summary of the electrochemical and spectral (visible, $^1$H NMR) properties for all the complexes reported in this study is given in Table 1.

*Electrochemical Studies.*—Cyclic voltammetry of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ in 0.1 mol dm$^{-3}$ HCl showed a reversible $Ru^{III}$–$Ru^{II}$ couple in the anodic region, with $E_{\frac{1}{2}}$ = 0.62 V. The $E_{\frac{1}{2}}$ value is pH-dependent over the range pH 1–6.5, and a plot of $E_{\frac{1}{2}}$ *vs.* pH is linear with a slope of 58 mV per pH unit. Such behaviour indicates a reversible deprotonation coupled with the electrode process, and has been observed previously for the $[Ru(L\text{–}L)_2(py)(OH_2)]^{3+/2+}$ couples (L–L = bipy[8] or 2-arylazopyridine,[9] py = pyridine), and in the present case is consistent with the reaction sequence (4) and (5). Furthermore,

$$[(bipy)_2Ru^{II}(NC_5H_4CH_2OH)]^{2+} \xrightarrow{-e^-} [(bipy)_2Ru^{III}(NC_5H_4CH_2OH)]^{3+} \quad (4)$$

$$[(bipy)_2Ru^{III}(NC_5H_4CH_2OH)]^{3+} \rightleftharpoons [(bipy)_2Ru^{III}(NC_5H_4CH_2O)]^{2+} + H^+ \quad (5)$$

the linearity of the plot throughout the pH region 1–6.5 implies the p$K_a$ of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{3+}$ must be $\leqslant 1$.[10] In the complex $[Ru(bipy)_2(py)(OH_2)]^{2+}$ the p$K_a$ of the aqua ligand decreases from 10.26 to 0.85 upon oxidation of the metal centre to the trivalent state.[8] The p$K_a$ of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ is 7.2, so that a similar decrease in the p$K_a$ of the alcohol ligand upon oxidation of the metal centre would indicate that the p$K_a$ of the ruthenium(III) complex may be $<0$, which is consistent with the electrochemical results.

Spectrocoulometry of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ in 0.1 mol dm$^{-3}$ $CF_3SO_3H$–0.9 mol dm$^{-3}$ NaCl solution at 0.65 V reveals a quantitative two-electron oxidation of the ligand (isosbestic points at 312, 385, 430 and 494 nm) to form the corresponding aldehyde complex $[Ru(bipy)_2(NC_5H_4CHO)]^{2+}$, identified by spectral comparisons with an authentic sample of that species (Fig. 2). The bleaching of the solution at coulometric $n > 2.0$ electrons is presumably due to formation of the ruthenium(III) species $[Ru(bipy)_2(NC_5H_4CHO)]^{3+}$.

*Chemical Oxidation Studies.*—The electrochemical results, and previously reported studies on the oxidation of the analogous amine complexes,[3,4] imply that the first step in the ligand oxidation reaction (2) is the one-electron oxidation of the metal centre, $Ru^{II} \longrightarrow Ru^{III}$. Of a number of chemical oxidants capable of promoting this step, $[Os(bipy)_3]^{3+}$ {$E_{\frac{1}{2}}$ for $[Os(bipy)_3]^{3+/2+}$ = 0.82 V in aqueous acidic solution} was chosen because of its stability in aqueous solution over the pH range studied (0–6), and because of the presumed rapidity of reaction (6). Although the rate of this electron transfer was not

$$[Os^{III}(bipy)_3]^{3+} + [(bipy)_2Ru^{II}(NC_5H_4CH_2OH)]^{2+} \longrightarrow [Os^{II}(bipy)_3]^{2+} + [(bipy)_2Ru^{III}(NC_5H_4CH_2OH)]^{3+} \quad (6)$$

measured directly, its order of magnitude can be estimated to be $> 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$.[11] {The rate of self exchange for $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{3+/2+}$ was assumed to be similar to that for $[Ru(bipy)_3]^{3+/2+}$ ($2 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$).[12a] The

**Table 2** Variation of the second-order rate constant $k_2$ for the oxidation of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ with base strength

| Base | $pK_a$ of conjugate acid * | $10^2k_2/dm^3\ mol^{-1}\ s^{-1}$ |
|---|---|---|
| Acetate | 4.56 | 25.1 |
| Formate | 3.56 | 12.9 |
| Chloroacetate | 2.64 | 5.2 |
| Dichloroacetate | 0.98 | 1.1 |

* Values determined within this work under the conditions of the kinetic experiments [$I$ = 1.0 mol $dm^{-3}$ (NaCl), 25.0 °C].

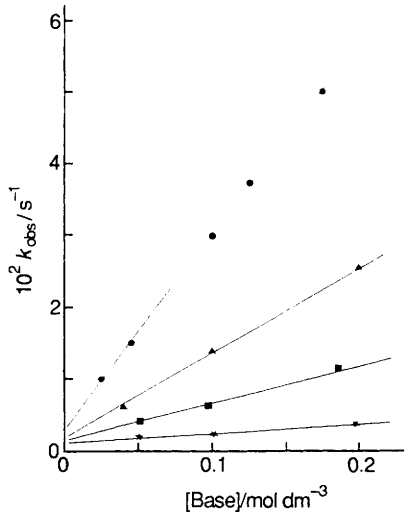



**Fig. 3** Variation in pseudo-first-order rate constant ($k_{obs}$) with base and [base] for the base-catalysed oxidation of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$: ●, acetate buffer; ▲, formate buffer; ■, chloroacetate buffer; ★, dichloroacetate buffer

self-exchange rate for $[Os(bipy)_3]^{3+/2+}$ was also assumed to be $2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$.[12b]

The stoichiometry of the reaction succeeding (6) is as in equation (7) and this could be followed spectrophotometrically

$$2[(bipy)_2Ru^{III}(NC_5H_4CH_2OH)]^{3+} \longrightarrow [(bipy)_2Ru^{II}(NC_5H_4CH_2OH)]^{2+} + [(bipy)_2Ru^{II}(NC_5H_4CHO)]^{2+} + 2H^+ \quad (7)$$

by monitoring the appearance of the aldehyde complex subsequent to the rapid formation of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{3+}$. The kinetics of formation of $[Ru(bipy)_2(NC_5H_4CHO)]^{2+}$ exhibited first-order behaviour, with $\log(A_\infty - A_t)$ *vs.* $t$ plots being linear for at least 3 half-lives. The rate constant was independent of the concentration of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$, but strongly dependent on pH, base strength and base concentration.

*Rate Studies in Buffer Solutions.—Variations of $k_{obs}$ with base and base concentration.* Rate studies of the oxidation reaction in the presence of a number of bases revealed general base catalysis of the process. Fig. 3 shows the dependence of $k_{obs}$ on acetate, formate, chloroacetate and dichloroacetate concentrations in buffer solutions at pH $\approx pK_a$ in each case. A second-order rate constant ($k_2$) corresponding to the base-assisted process could be calculated for each set of buffers from the slope of these lines (Table 2). The variation of the intercepts with the various bases is consistent with the rate at the corresponding pH of a parallel base-independent pathway, which was studied by use of pH-stat techniques (see later).

For a general base-catalysed reaction involving the transfer of one proton the Brønsted catalysis law[13] requires the proportionality of $\log k_2$ and $pK_a$: in the present case a plot of the data from Table 2 gives a straight line of slope $\beta = 0.4$, indicating general base catalysis involving an essentially symmetrical transition state.[14]

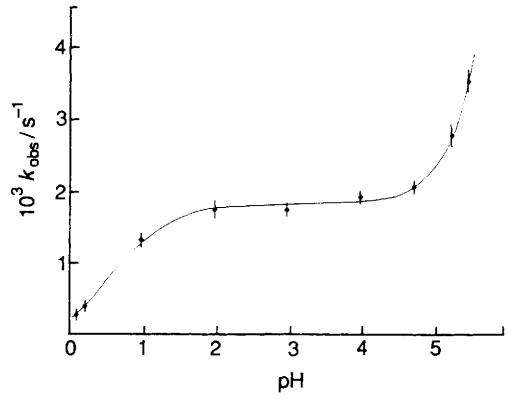



**Fig. 4** Variation in pseudo-first-order rate constant ($k_{obs}$) with pH for the base-independent oxidation of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$

Comparative rate studies of the oxidation of $[(Ru(bipy)_2(NC_5H_4CD_2OH)]^{2+}$ reveal a kinetic isotope effect $k_H/k_D = 9$, which clearly demonstrates that the C–H bond is broken in the rate-determining step. The value of the kinetic isotope effect is sensitive to the symmetry of the transition state,[15] a large value being interpreted to indicate a symmetrical transition state, which verifies the conclusions based on the value of $\beta$.

The general base catalysis is presumed to be associated with base-assisted removal of the methylene (or methine) proton from the $\alpha$-carbon atom in the rate-determining step.[4]

*Variation of $k_{obs}$ with* pH.—A kinetic study of the oxidation of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ was undertaken in the range pH 0–5.5 using pH-stat facilities (NaOH titrant) in conjunction with spectrophotometric measurements. The pH-stat results revealed that one $H^+$ per $Os^{III}$ was produced during the oxidation reaction and that the uptake of NaOH was primarily associated with the mixing of the ruthenium(II) and osmium(III) reactants, and not with the subsequent slower formation of the $[Ru(bipy)_2(NC_5H_4CHO)]^{2+}$ product.

For the intramolecular redox process the spectrophotometric studies of the rate of formation of the product revealed linear $\log(A_\infty - A_t)$ *vs.* $t$ plots for 3 half-lives, and the pH-rate profile is given in Fig. 4. The curve shows an increase in $k_{obs}$ from pH 0 to 2, followed by a pH-independent region between pH 2 and 5, with a subsequent rapid increase in rate above pH 5.

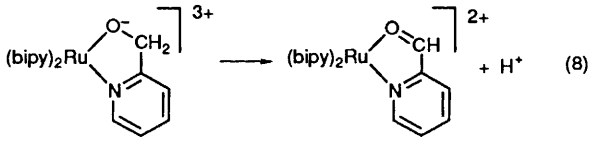
A deuterium isotope-exchange study, in which the oxidation of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ was undertaken in $D_2O$ solution, revealed the formation of $[Ru(bipy)_2(NC_5H_4CHO)]^{2+}$ only, so that no exchange at the methylene carbon atom occurs during the reaction.

*Mechanism of Oxidative Dehydrogenation.*—There have been a number of mechanistic studies of ligand oxidations, and in particular of co-ordinated amines. A common feature is that initial oxidation occurs at the metal centre with oxidative dehydrogenation of the ligand taking place in a subsequent intramolecular redox process. There are two commonly accepted alternative paths for this latter process. The first involves the intermediacy of a *ligand radical* species, and this has been identified in studies of the oxidations of nickel(II) complexes of a variety of macrocycles,[16–18] $[Fe(CN)_4(en)]^-$ (en = ethane-1,2-diamine),[19] and $[Fe(tacn)_2]^{3+}$ (tacn = 1,4,7-triazacyclononane).[20] The second alternative invokes *disproportionation* at the metal centre to form an oxidation state two units higher than the final state, allowing two-electron oxidation of the ligand with concomitant two-electron reduction of the metal. Detailed mechanistic studies of ligand oxidation in $[Ru(bipy)_2(NC_5H_4CH_2NH_2)]^{2+}$ [$NC_5H_4CH_2NH_2$ = 2-(aminomethyl)-

pyridine] and analogues (from our laboratories),[3,4] $[Os(en)_3]^{2+}$ (by Lay *et al.*[21]) and $[Ru(hbi)]^{2+}$, $[Ru(en)_3]^{2+}$ and $[Ru(tame)_2]^{2+}$ complexes {hbi = 3,6,10,13,16,19-hexaazabicyclo-[6.6.6]icosane; tame = 1,1,1-tris(aminomethyl)ethane} by Bernhard, Bull and Sargeson[22,23] have identified these disproportionation processes: the substantial stabilization of the higher oxidation states of their complexes by ligand deprotonation is a significant factor contributing to the particular ability of ruthenium and osmium to promote such reactions by this pathway.

In light of the results of the closely related studies on oxidative dehydrogenation reactions involving analogous amine complexes, the intermediacy of the ruthenium(IV)–alkoxide species, $[Ru(bipy)_2(NC_5H_4CH_2O)]^{3+}$, in the oxidation of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ seemed likely. Two additional observations favour this hypothesis. First, the presence of a vast excess ($\times 10^4$) of the radical scavenger acrylamide had no effect on the rate of the oxidation reaction (carried out at pH 3), and no polymerization occurred. It is therefore unlikely that the oxidation mechanism involved a ligand radical species, as required for the intermediacy of a ruthenium(III) complex. Secondly, a study of the variation of the rate of the oxidation process with ionic strength ($I$) was undertaken at low $I$ (< 0.04 mol $dm^{-3}$). According to the Brønsted–Bjerrum relationship[24] between $k_{obs}$ and ionic strength, $\log(k_{obs}) = \log k_0 + 1.02 Z_A Z_B I^{\frac{1}{2}}$ where $k_0$ = rate constant at infinite dilution, $Z_A$ and $Z_B$ are the charges on the reacting species, a plot of $\log(k_{obs})$ *vs.* $I^{\frac{1}{2}}$ at pH 4.41 in acetate buffer solution revealed a linear relationship with a slope of −2.8. This result is interpreted to indicate that the charge on the metal complex involved in the base-catalysed reaction must be +3.

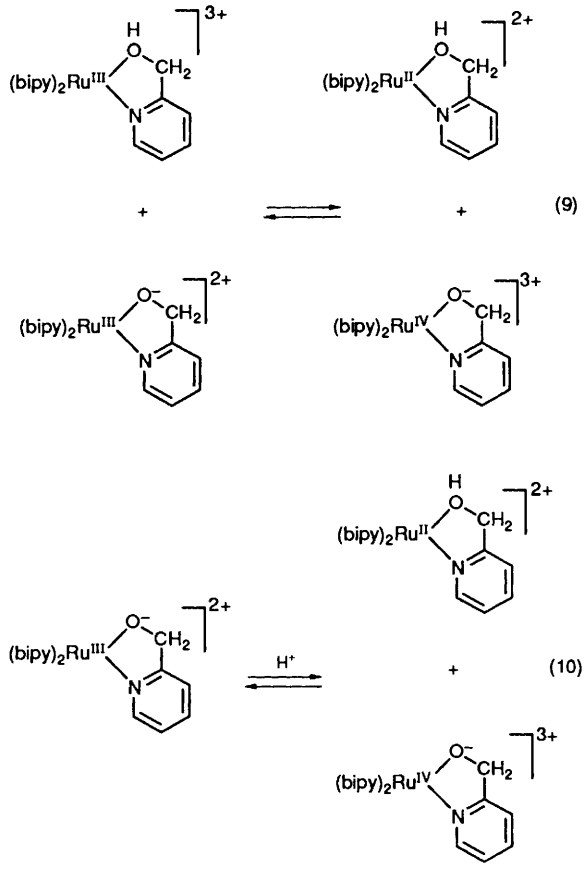
Over the range pH 2–5 the observations are consistent with the rapid formation of a ruthenium(III)–alcohol species which is immediately deprotonated, $pK_a \approx 1$. A rapid disproportionation process follows in which the intermediate $[Ru^{IV}(bipy)_2(NC_5H_4CH_2O)]^{3+}$ is formed, which then undergoes the observed first-order decay to the aldehyde product. Accordingly, the rate-determining step of the reaction may be written as in equation (8). In the absence of any other oxidizing species, the




(8)

ruthenium(IV) complex may only arise from the disproportionation of two ruthenium(III) species, as described for the analogous amine species.[3,4]

Additionally, in their study of the oxidation of the alcohol complex $[Ru(NH_3)_4\{NC_5H_4CH(CH_3)OH\}]^{2+}$, Tovrog *et al.*[2] showed that on raising the pH of the solution of the ruthenium(III)–alcohol complex, equimolar amounts of the ruthenium(II)–alcohol and –ketone complexes formed. They suggested the involvement of a ruthenium(IV)–alkoxide species formed upon disproportionation of two ruthenium(III)–alcohol molecules. A similar experiment was undertaken with $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$. A solution of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ in 1.0 mol $dm^{-3}$ was electrolysed at 650 mV [*vs.* saturated sodium chloride calomel electrode (SSCE)] to yield an essentially colourless solution of the ruthenium(III)–alkoxide complex, $[Ru(bipy)_2(NC_5H_4CH_2O)]^{2+}$. This formulation could be verified as the electrolysis corresponded to $1e^-$ per $Ru^{II}$ and by the quantitative re-reduction of the ruthenium(III) species to the ruthenium(II) complex by electrolysis at 0.50 V (*vs.* SSCE). Additionally, there are close electronic spectral similarities between the ruthenium(III) complex ($\lambda_{max}$ = 375 nm, $\varepsilon$ = 4000 $dm^3$ $mol^{-1}$ $cm^{-1}$) and $[Ru(bipy)_2(py)(OH)]^{2+}$ (ref. 8) ($\lambda_{max}$ = 364 nm, $\varepsilon$ = 4700 $dm^3$ $mol^{-1}$ $cm^{-1}$). Dilution of the electrogenerated complex (20:1) with deaerated 1 mol $dm^{-3}$ NaCl resulted in the gradual formation of an absorbance at 482 nm. A




plot of $\log(A_\infty - A_t)$ *vs.* $t$ for this reaction showed $k_{obs}$ = 1.1 × $10^{-3}$ $s^{-1}$ at pH 1.3, which is very similar to the observed rate for the osmium(III)-promoted oxidation of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ at the same pH to form the same product. This behaviour is consistent with a disproportionation reaction between two ruthenium(III) species to form a ruthenium(IV) complex. The disproportionation reaction would be written either as in equation (9) or (10) depending on the pH of the solution.

The observed first-order behaviour requires that by the time the first point is recorded effectively complete formation of the ruthenium(IV) species has occurred, otherwise second-order terms in $[Ru^{III}]$ would be observed. Hence, $E_{\frac{1}{2}}$ of the redox couple $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{3+/2+}$ must be anodic of that for $[Ru(bipy)_2(NC_5H_4CH_2O)]^{3+/2+}$. Such an observation is not without precedence. The $Ru^{IV}$–$Ru^{III}$ couple of $[RuL_2(py)(OH)]^{n+}$ (L = 2-phenyl- or 2-tolyl-azopyridine) is cathodic of the $Ru^{III}$–$Ru^{II}$ couple of $[RuL_2(py)(OH_2)]^{n+}$,[9] and in our previous studies of the oxidation of the $[Ru(bipy)_2(NC_5H_4CH_2NH_2)]^{2+}$ the $E_{\frac{1}{2}}$ of the deprotonated $Ru^{IV}$–$Ru^{III}$ couple was deduced to be cathodic of the non-deprotonated $Ru^{III}$–$Ru^{II}$ couple.[3] Another example of such behaviour was reported in studies of the oxidation of $[Ru(terpy)(bipy)(NH_2Pr^i)]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) where it was found that $E_{pa}$ for the $Ru^{IV}$–$Ru^{III}$ couple of $[Ru(terpy)(bipy)(N{=}CMe_2)]^{n+}$ (imine ligand deprotonated) was 0.34 V cathodic of $E_{pa}$ for the $Ru^{III}$–$Ru^{II}$ couple of $[Ru(terpy)(bipy)(NH{=}CMe_2)]^{n+}$ (imine ligand non-deprotonated).[25] The pronounced stabilization of higher oxidation states of ruthenium by ligand deprotonation is a consequence of substantial ligand-to-metal $\pi$ bonding, and has been discussed previously.[3,4,25]

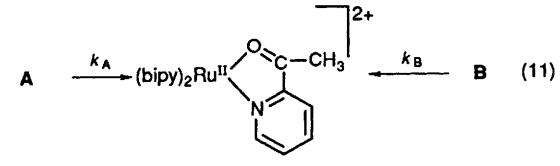
It is interesting that whereas the kinetics of formation of the aldehyde product is first order, the analogous formation of the imine product from the amine complex $[Ru(bipy)_2(NC_5H_4CH_2NH_2)]^{2+}$ was observed to have considerable second-order characteristics.[3] Given that the rates of the preliminary protonic

and disproportionation processes are comparable in the two cases, the difference between the amine and alcohol species is a consequence of the stability and substantially slower dehydrogenation of the ruthenium(IV)–alkoxide intermediate relative to its ruthenium(IV)–amide counterpart.

In an attempt to isolate a ruthenium(IV) complex analogous to that inferred from the kinetic considerations above, $[Ru(bipy)_2\{NC_5H_4C(CH_3)_2OH\}]^{2+}$ was synthesized. This complex would not be expected to undergo ligand dehydrogenation because of the dimethylation at the α-carbon atom. It was hoped that should the $Ru^{IV}$–$Ru^{III}$ couple of the deprotonated alcohol $[Ru(bipy)_2\{NC_5H_4C(CH_3)_2O\}]^{3+/2+}$ be cathodic of the $[Ru(bipy)_2\{NC_5H_4C(CH_3)_2OH\}]^{3+/2+}$ couple, then exhaustive electrolysis of a solution of $[Ru(bipy)_2\{NC_5H_4C(CH_3)_2OH\}]^{2+}$ would yield a ruthenium(IV) complex with a coulometric $n = 2$. The alcohol complex shows a reversible cyclic voltammetric couple, but exhaustive electrolysis at a potential anodic of this couple resulted in $n = 1$ at pH 1 and 4, indicating formation of the ruthenium(III) species. The failure to produce $[Ru(bipy)_2\{NC_5H_4C(CH_3)_2O\}]^{3+}$ directly may be interpreted to show the sensitivity of the $Ru^{IV}$–$Ru^{III}$ redox couple in these complexes to the variation of ligand environment around the metal centre: in this case the steric consequences of dimethylation at the α-carbon atom of the chelate ring may destabilize the ruthenium(IV)–alkoxide species.

*The Relative Rate of Oxidation of the Two Diastereoisomers of* $[Ru(bipy)_2\{NC_5H_4C(CH_3)OH\}]^{2+}$.—The complex $[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}]^{2+}$ exists in two diastereoisomeric pairs, in which the α-methyl group is either axial or equatorial to the mean plane of the chelate ring. It was possible to separate the two diastereoisomers partially by repeated fractional crystallization of the iodide salt, with the ultimate ratios **A**:**B** in the final enriched samples being 86:14 and 22:78, determined by integration of the separate methyl resonances in an $^1H$ NMR spectrum of each of the samples.

Kinetic studies of the oxidation of the two diastereoisomers were undertaken on these enriched samples: since the ketone produced by the oxidation is non-chiral, the same product is obtained by the oxidation of both diastereoisomers **A** and **B**. The kinetics of oxidation of **A** and **B** therefore exhibited the behaviour of two competing parallel reactions, as is shown in equation (11). The rates of oxidation of the two enriched



(11)

samples were measured in acetate buffer solutions, and knowing the relative proportions of **A**:**B** in the two samples the rate constants $k_A$ and $k_B$ were determined[26] to be 0.018 and 0.19 $dm^3\ mol^{-1}\ s^{-1}$. The ten-fold variation between **A** and **B** for the acetate-catalysed oxidation process confirms that C–H bond cleavage is involved in the rate-determining step and shows that this cleavage is sensitive to the stereochemical environment of the methine carbon.

For the corresponding amine complexes involving the ligand $NC_5H_4CH(CH_3)NH_2$ there was little difference in the rates of oxidation of the two diastereoisomers.[4] Interestingly, the relative rates of oxidation for the two diastereoisomer stereochemistries were reversed for the alcohol and amine analogues. In the present instance of the alcohol complex the origins for the different rates of oxidation of **A** and **B** are a difference in the acidity of the methine proton in the two diastereoisomers and/or stereochemical effects. If the explanation were the former and a common mechanism applies for the oxidation of the two diastereoisomers, then the acidity of the methine proton of **B** is one $pK_a$ unit less than that of **A** given the ten-fold difference in the oxidation rates. On the other hand, the difference in rates may reflect the orientation of the methine proton (axial or equatorial) within the ruthenium(IV)–alkoxide intermediate and its accessibility to approach by the abstracting base. While it is clear that in the ruthenium(II) complexes, where the ligand is not deprotonated, the more rapidly oxidized diastereoisomer **B** has a clear equatorial orientation of the methine proton, no conclusion can be drawn for the ruthenium(IV) intermediate since in the latter case the alcohol OH group would be deprotonated and the anticipated substantial π interaction between the metal centre and the alkoxide group would lead to significant changes in the stereochemistry of the chelate ring.

## Experimental

*Measurements.*—Electronic spectra were recorded on a Cary 219 spectrophotometer, NMR spectra using either a JEOL FX90Q or a Bruker AM-300 spectrometer; resonances are quoted relative to $SiMe_4$ as an internal reference.

All electrochemical measurements were made (and are quoted) *vs.* the SSCE and are uncorrected for junction potentials. Cyclic voltammetry experiments were performed using a Bioanalytical Systems (BAS) CV-27 Voltammograph, or a Utah Electronics 0152 potentiostat coupled to a 0151 sweep generator, and output on a Rikadenki RW-101 or a Linseis LY-1800 X-Y recorder. Coulometry experiments were made using the BAS Voltammograph. Temperature control for electrochemical experiments was achieved with a Lauda K4RD circulating water-bath (25.00 ± 0.05 °C).

Elemental analyses were carried out by the Australian Microanalytical Service, AMDEL, Melbourne.

*Materials.*—Tetraethylammonium perchlorate, used as an electrolyte for electrochemical measurements, was prepared and purified by standard techniques.[27] 2-Acetyl- and 2-(hydroxymethyl)-pyridine (Fluka) were used as received, and pyridine-2-carbaldehyde (Sigma) and 2-bromopyridine (Fluka) were distilled prior to use. Propylene carbonate (Aldrich) was distilled immediately before use (90–92 °C, 3–3.5 mmHg) and stored over 4 Å molecular sieves. Ammonium cerium sulfate (Fluka, puriss) was standardized and found to be $(NH_4)_4Ce(SO_4)_4 \cdot H_2O$. All other chemicals were AR grade where available and were used without further purification. Tetrahydrofuran (thf) was distilled from sodium.

*Syntheses.*—The compounds $[Ru(bipy)_2Cl_2]\cdot 2H_2O$,[28] $[Ru(bipy)_2(CO_3)]\cdot 2H_2O$,[29] $[Os(bipy)_3][ClO_4]_2\cdot 2H_2O$,[30] pyridine-2-carboxylic acid[31] and 2-(1-hydroxyethyl)pyridine[32] were synthesized by literature methods.

2-(*Dideuteriohydroxymethyl*)*pyridine*, $NC_5H_4CD_2OH$. The compound $LiAlD_4$ (0.9 g) was suspended in freshly distilled dry thf (15 $cm^3$) under $N_2$. Pyridine-2-carboxylic acid (0.8 g) dissolved in thf (10 $cm^3$) was added dropwise with stirring, and the solution was refluxed for 24 h. After cooling, water (0.9 $cm^3$), 15% aqueous NaOH (2.5 $cm^3$) and water (0.9 $cm^3$) were sequentially added and the solution filtered. The precipitate was washed with diethyl ether, and the filtrate extracted with ether, and the combined organic extracts dried over anhydrous $Na_2SO_4$. After filtration, the solvent was removed by evaporation at reduced pressure to yield the crude product (0.8 g, 90%), which was used directly for complex formation.

2-(2-*Pyridyl*)*propan*-2-*ol*, $NC_5H_4C(CH_3)_2OH$. Freshly distilled 2-bromopyridine (3.5 $cm^3$, 0.030 mol) in dry ether (40 $cm^3$) was added rapidly dropwise to a stirred solution of $LiBu^n$ (25.5 $cm^3$, 1.40 mol $dm^{-3}$) cooled to −60 °C, giving a deep red solution. The mixture was stirred for 15 min and a solution of acetone (3.0 $cm^3$, 0.052 mol) in ether (20 $cm^3$) and thf (20 $cm^3$) was added dropwise. The mixture was stirred for 1 h, then allowed to warm to room temperature. The red solution was acidified (2.5 mol $dm^{-3}$ $H_2SO_4$) and the ether layer extracted with 2.5 mol $dm^{-3}$ $H_2SO_4$ (3 × 30 $cm^3$). The combined acid

extracts were basified using NaOH, and the mixture extracted with ether. The organic extract was dried over anhydrous $Na_2SO_4$, and the solvent evaporated. The product was distilled under reduced pressure (b.p. 77 °C, 7 mmHg); yield 2.2 g, 45%; m.p. 50 °C (lit.,[33] 50–51 °C). The $^1H$ NMR spectrum ($CDCl_3$) showed δ 1.55 ($CH_3$) and 5.00 (–OH).

*Bis*(2,2′-*bipyridine*)[2-(*hydroxymethyl*)*pyridine*]*ruthenium*(II) *hexafluorophosphate*, $[Ru(bipy)_2(NC_5H_4CH_2OH)][PF_6]_2$ **1a**. 2-(Hydroxymethyl)pyridine (2.2 g, 20 mmol) was added to a deaerated refluxing solution of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (550 mg, 1.05 mmol) in water–methanol solution (1:1, 30 $cm^3$). After the solution had been refluxed for 40 min under a nitrogen atmosphere, 75% $HPF_6$ (2.5 $cm^3$) was added, the condenser removed, and the methanol boiled off. The solution was cooled, filtered, and the product washed with ice-cold 0.1 mol $dm^{-3}$ HCl and dried *in vacuo*. The complex was dissolved in 0.01 mol $dm^{-3}$ HCl and sorbed onto a column packed with SP-Sephadex C-25 cation exchanger; on elution with 0.5 mol $dm^{-3}$ NaCl–0.01 mol $dm^{-3}$ HCl the second (major) band was collected. The product was precipitated by the addition of $NH_4PF_6$, filtered off, washed with 0.1 mol $dm^{-3}$ HCl, and dried *in vacuo*. Yield 580 mg, 68% (Found: C, 37.7; H, 2.95; N, 8.3. $C_{26}H_{23}F_{12}N_5OP_2Ru$ requires C, 38.4; H, 2.85; N, 8.6).*

Bis(2,2′-bipyridine)[2-(dideuteriohydroxymethyl)pyridine]-ruthenium(II) hexafluorophosphate, $[Ru(bipy)_2(NC_5H_4CD_2OH)][PF_6]_2$ **1b** was prepared in an analogous manner (Found: C, 38.4; H, 3.10; N, 8.7. $C_{26}H_{21}D_2F_{12}N_5OP_2Ru$ requires C, 38.3; H/D, 3.10; N, 8.5%).

Bis(2,2′-bipyridine)[2-(1-hydroxyethyl)pyridine]ruthenium-(II) hexafluorophosphate, $[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}][PF_6]_2$ **1c**, was prepared in 70% yield by a similar method (Found: C, 37.7; H, 3.10; N, 8.4. $C_{27}H_{25}F_{12}N_5OP_2Ru$ requires C, 37.7; H, 3.25; N, 8.4%). This complex exists as two diastereoisomeric pairs which could be obtained in *ca.* 80–85% enrichment by repeated fractional crystallizations as the iodide salt. Attempts to separate the two diastereoisomers chromatographically in an analogous manner to that for the amine analogues[4] were unsuccessful because of gradual oxidation of the complex under the conditions (pH 3, 4 °C) in the time-scale of the separation (weeks). The separation of the two diastereoisomers was monitored by $^1H$ NMR spectroscopy in $(CD_3)_2SO$: the diastereoisomer which formed the less-soluble iodide (**A**) showed a doublet resonance centred at δ 1.25 due to the methyl group, compared with δ 1.73 observed for the more-soluble diastereoisomer (**B**). Ultimate ratios **A**:**B** in the final enriched samples were 86:14 and 22:78.

Bis(2,2′-bipyridine)[2-(2-pyridyl)propan-2-ol]ruthenium(II) hexafluorophosphate, $[Ru(bipy)_2\{NC_5H_4C(CH_3)_2OH\}][PF_6]_2$ **1d**, was prepared and purified in an analogous manner (Found: C, 40.5; H, 3.35; N, 8.1. $C_{28}H_{27}F_{12}N_5OP_2Ru$ requires C, 40.0; H, 3.25; N, 8.3%).

*Bis*(2,2′-*bipyridine*)*bis*(*trifluoromethanesulfonato*)*ruthenium*-(II), $[Ru(bipy)_2(O_3SCF_3)_2]$. The compound $[Ru(bipy)_2(CO_3)]\cdot 2H_2O$ (200 mg) was suspended in 1,2-dimethoxyethane (10 $cm^3$), trifluoromethanesulfonic acid (0.5 $cm^3$) was added slowly with stirring, and the solution cooled and maintained at 0 °C overnight. The precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 140 mg, 75%.

*Bis*(2,2′-*bipyridine*)(*pyridine*-2-*carbaldehyde*)*ruthenium*(II) *hexafluorophosphate*, $[Ru(bipy)_2(NC_5H_4CHO)][PF_6]_2$, **2a**. The compound $[Ru(bipy)_2(O_3SCF_3)_2]$ (200 mg) was suspended in a freeze-thaw-degassed solution of freshly distilled ligand (0.2 g, seven-fold molar excess) in dichloromethane (10 $cm^3$), and the mixture stirred in the dark on a vacuum line for 12 h. The vacuum was released, and the solution rapidly extracted with an aqueous 1% $HPF_6$ solution to remove the excess of ligand. The dichloromethane layer was evaporated to dryness (rotary evaporator), and the residue dissolved in 5 × $10^{-3}$ mol $dm^{-3}$ HCl (25 $cm^3$) by stirring with Dowex 1 × 8 resin ($Cl^-$ form). This solution was sorbed onto a column of SP-Sephadex C-25 cation exchanger and eluted with 0.5 mol $dm^{-3}$ NaCl–5 × $10^{-3}$ mol $dm^{-3}$ HCl. The second (major) band was collected and the complex precipitated by addition of $NH_4PF_6$. The precipitate was filtered off, washed with ice-cold 0.1 mol $dm^{-3}$ HCl and dried *in vacuo*. Yield 183 mg, 80% (Found: C, 37.8; H, 2.70; N, 8.7. $C_{26}H_{21}F_{12}N_5OP_2Ru$ requires C, 38.5; H, 2.80; N, 8.6%).

(2-Acetylpyridine)bis(2,2′-bipyridine)ruthenium(II) hexafluorophosphate, $[Ru(bipy)_2\{NC_5H_4C(CH_3)O\}][PF_6]_2$ **2b**, was prepared and purified in an analogous manner (Found: C, 39.1; H, 2.90; N, 11.9. $C_{27}H_{23}F_{12}N_5OP_2Ru$ requires C, 39.3; H, 3.00; N, 11.8%).

*Bis*(2,2′-*bipyridine*)(*pyridine*-2-*carboxylato*)*ruthenium*(II) *hexafluorophosphate*, $[Ru(bipy)_2(NC_5H_4CO_2)]PF_6$ **3**. This was prepared in an analogous manner to that for $[Ru(bipy)_2(NC_5H_4CH_2OH)][PF_6]_2$. The complex was chromatographed as for $[Ru(bipy)_2(NC_5H_4CHO)][PF_6]_2$ and the first band collected (Found: C, 45.7; H, 3.00; N, 10.1. $C_{26}H_{20}F_6N_5O_2PRu$ requires C, 45.8; H, 2.95; N, 10.3%).

*Stoichiometry and Equilibrium Studies.—Spectrocoulometric titration of the oxidation of* $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$. A solution of $[Ru(bipy)_2(NC_5H_4CH_2OH)][PF_6]_2$ (50 $cm^3$, 3.123 × $10^{-4}$ mol $dm^{-3}$ in 0.1 mol $dm^{-3}$ $CF_3SO_3H$–0.9 mol $dm^{-3}$ NaCl) was placed in the working electrode compartment of a conventional three-compartment electrochemical cell. The solution was deaerated with Ar† and the potential of the working electrode set to 0.65 V by use of a coulometer. By taking samples, the electronic spectra of the initial solution and of the solution after oxidation corresponding to 0.5, 1.0, 1.5 and 1.99 $e^-$ per molecule of Ru were recorded. The working electrode potential was increased to 0.80 V and a current corresponding to a further 0.5 $e^-$ per molecule Ru was passed at which time the solution spectrum was again recorded.

*Determination of the* $pK_a$ *of* $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$, $[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}]^{2+}$ *and* $[Ru(bipy)_2\{NC_5H_4(CH_3)_2OH\}]^{2+}$. The $pK_a$ values for $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ and $[Ru(bipy)_2\{NC_5H_4CH(CH_3)OH\}]^{2+}$ in 0.1 mol $dm^{-3}$ $LiNO_3$ solution and of $[Ru(bipy)_2\{NC_5H_4C(CH_3)_2OH\}]^{2+}$ in 0.1 mol $dm^{-3}$ $KNO_3$ solution were determined at 25.0 °C by an automated titration system which has been described elsewhere.[36] In all cases the reported value is the average of two runs.

*Determination of the equilibrium constant for hydrate formation of* $[Ru(bipy)_2(NC_5H_4CHO)]^{2+}$. An argon-deaerated solution of $[Ru(bipy)_2(NC_5H_4CHO)][PF_6]_2$ (35 $cm^3$, 1.12 × $10^{-5}$ mol $dm^{-3}$ in $10^{-4}$ mol $dm^{-3}$ HCl–1.0 mol $dm^{-3}$ NaCl) was placed in the titrating compartment of a Radiometer ETS 882 end-point titrating system. This solution was circulated through a 1 cm path length cell in the cell compartment of a Cary 219 spectrophotometer by use of a Gilson Minipuls 2 peristaltic pump. The pH was adjusted to the desired value over the range 5–11 by addition of 0.01 mol $dm^{-3}$ NaOH–0.99 mol $dm^{-3}$ NaCl, and the optical density of the solution measured at 435 and 505 nm. The equilibrium constant of the complex was calculated by a similar technique to that described by Ford and co-workers[5] for the analogous $[Ru(NH_3)_4(NC_5H_4CHO)]^{2+}$ system.

* For some complexes in this study, microanalytical features were persistently low for C. In such cases, characterization and purity assessment were made on the basis of NMR spectra, electrochemical behaviour, and ion-exchange chromatography.

† All electrochemical and kinetic measurements were conducted in argon-deaerated media due to the potential sensitivity to oxygen of the alcohol complexes. Argon was scrubbed of $O_2$ by passing through either a column packed with BTS catalyst (Fluka) at 180 °C[34] or a chromium(II) solution.[35]

*Deuterium Exchange Studies.*—A solution of $[Ru(bipy)_2(NC_5H_4CD_2OH)][PF_6]_2$ (45.3 mg, 0.056 mmol) in 0.5 mol $dm^{-3}$ $H_2SO_4$ was deaerated, and a solution of $(NH_4)_4Ce(SO_4)_4 \cdot H_2O$ in the same solvent (4.67 $cm^3$ of 0.119 mol $dm^{-3}$, 0.056 mmol) was added. The solution was allowed to stand until no further reaction occurred (*ca.* 4 h) and then the complex was precipitated by the addition of excess of solid $NH_4PF_6$. The precipitate (a mixture of the reactant alcohol and product aldehyde complexes) was filtered off, washed with ice-cold 0.1 mol $dm^{-3}$ HCl, and dried *in vacuo*. The $^1H$ NMR spectrum of the dried solid was measured in $(CD_3)_2SO$.

*Kinetic Studies.*—Solutions of $[Os(bipy)_3]^{3+}$ were electrogenerated immediately prior to use by exhaustive electrolysis of a solution of $[Os(bipy)_3][ClO_4]_2 \cdot 2H_2O$ in the medium to be studied ($I$ = 1.0 mol $dm^{-3}$, NaCl) at 0.9 V. These solutions and $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ solutions were deaerated (Ar) and thermostatted before mixing.

*Stopped-flow studies using buffer* pH *control.* The ruthenium(II) and osmium(III) solutions were mixed using a hand-operated stopped-flow device constructed in the Department. The mixed solution passed into a 1 cm path length flow-through cell placed in the cell compartment of a Cary 219 spectrophotometer. The cell block was thermostatted to 25.0 °C and the cell compartment was maintained under an argon atmosphere to minimize oxygen leakage through the tubing used to connect the mixing device with the cell. The reaction was monitored at 482 and/or 467 nm.

In a typical experiment, a solution of $[Ru(bipy)_2(NC_5H_4CH_2OH)][PF_6]_2$ ($4.97 \times 10^{-5}$ mol $dm^{-3}$) dissolved in 0.1 mol $dm^{-3}$ acetate buffer ($I$ = 1.0 mol $dm^{-3}$, NaCl) was mixed with a $1.75 \times 10^{-5}$ mol $dm^{-3}$ solution of $[Os(bipy)_3]^{3+}$ in the same medium. For a given set of conditions (pH, buffer type, buffer concentration) a minimum of three runs were recorded and the average value from these runs used in the calculations. The pH values of the solutions were measured before and after the oxidation reaction with a Radiometer PHM82 standard pH meter to ensure that adequate pH control was maintained during the reaction.

*Studies using* pH*-stat control.* The pH was maintained using a Radiometer ETS 822 end-point titration system. An aliquot (20 $cm^3$) of $[Ru(bipy)_2(NC_5H_4CH_2OH)]^{2+}$ ($4 \times 10^{-5}$ mol $dm^{-3}$) in $10^{-4}$ mol $dm^{-3}$ HCl–1.0 mol $dm^{-3}$ NaCl was placed in a thermostatted titration vessel. After deaeration, a 1 $cm^3$ aliquot of freshly generated $[Os(bipy)_3]^{3+}$ solution ($2 \times 10^{-4}$ mol $dm^{-3}$ in $10^{-4}$ mol $dm^{-3}$ HCl–1.00 mol $dm^{-3}$ NaCl) was added and the solution adjusted to the desired pH by the addition of 0.01 mol $dm^{-3}$ NaOH–0.99 mol $dm^{-3}$ NaCl using the titration system. The solution was maintained under a blanket of Ar and circulated through a 1 cm path length cell in the cell compartment of a Cary 219 spectrophotometer using a Gilson Minipuls 2 peristaltic pump, while the pH was maintained by the titration system.

*Variation of rate with ionic strength.* The stopped-flow technique used for kinetic runs studied under buffer pH-control was described earlier. A series of acetate buffer solutions ($[acetate]_{total}$ = 0.004 mol $dm^{-3}$, pH 4.41) was prepared in which the ionic strength was varied from $4 \times 10^{-3}$ to 0.034 mol $dm^{-3}$ by the addition of appropriate amounts of NaCl. The pH of the reaction solution was measured before and after mixing.

## Acknowledgements

This work was supported by the Australian Research Council. The assistance of Mr. A. J. Leong with the measurement of the $pK_a$ values for the alcohol complexes, and Dr. A. R. Carroll with the NOE/NMR studies, is very gratefully acknowledged.

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*Received* 23*rd January* 1992; *Paper* 2/00364C