Chemistry of Ruthenium. Part 9.† Electrophilic Addition of a Ruthenium Nitrosyl Complex to Alkylidenearylhydrazones. Arylazo-oximates of Bis(2,2′-bipyridyl)ruthenium(II)

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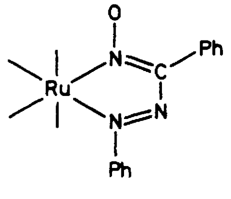
The electrophilic addition of $[\mathrm{Ru(bipy)_2(NO)Cl}][\mathrm{ClO_4}]_2$ to alkylidenearylhydrazones, RCH=NNHR′ (R = Me, Ph, or C_6H_4Me-*p*; R′ = Ph or C_6H_4Me-*p*) in methanol containing sodium methoxide affords the new complex $[\mathrm{Ru(bipy)_2(A)}][\mathrm{ClO_4}]\cdot H_2O$ (2) [HA = RC(=NOH)N=NR′; bipy = 2,2′-bipyridyl]. An alternative synthesis of (2) is provided by the reaction of *cis*-$[\mathrm{Ru(bipy)_2Cl_2}]$ with NaA. The protonation of (2) by $HClO_4$ in methanol gives $[\mathrm{Ru(bipy)_2(HA)}][\mathrm{ClO_4}]_2\cdot H_2O$ (5). The proton dissociation constants (p*K*) of (5) and of HA in dioxan–water (1 : 1) are respectively *ca.* 10 and *ca.* 3. All complexes display a ν(NO) of the arylazo-oximate chelate ring at *ca.* 1 240 cm^{-1} in the i.r. and one or more t_2(ruthenium) $\longrightarrow$ π^*(ligand) charge-transfer transition(s) in the visible region, 400—500 nm. A quasi-reversible Ru$^{\mathrm{III}}$–Ru$^{\mathrm{II}}$ couple occurs in (2) near 0.8 V *versus* s.c.e. with ΔE_p *ca.* 75 mV (cyclic voltammetry in acetonitrile). The Ru$^{\mathrm{III}}$ species $[\mathrm{Ru(bipy)_2(A)}]^{2+}$ is unstable and generally decomposes with a pseudo-first-order rate constant of 0.4—0.6 s^{-1} (298 K). In (5) the Ru$^{\mathrm{III}}$–Ru$^{\mathrm{II}}$ couple is at *ca.* 1.0 V.

Oximes are versatile ligands[1] for transition-metal ions but little was known about the oximates of ruthenium until recently.[2-7] A recognised but sparingly used [4,6,7] route for the synthesis of ruthenium oximates is the electrophilic addition of species having the $[\mathrm{Ru(NO)}]^{3+}$ moiety to a suitably activated carbon atom. This approach has thus far been limited [4,6,7] to the ${}^{-}\mathrm{COCH_2}{}^{-}$ function only [equation (i)]. In this work we successfully explore the synthesis of arylazo-oximates of bis(2,2′-bipyridyl)ruthenium(II) using the new nitrosation reaction between alkylidenearylhydrazones and $[\mathrm{Ru(bipy)_2(NO)Cl}]^{2+}$ (bipy = 2,2′-bipyridyl). The chelates have been

$$[\mathrm{Ru(NO)}]^{3+} + {}^{-}\mathrm{COCH_2}{}^{-} \longrightarrow \left[\underline{\mathrm{RuN(O){=}\overset{|}{C}{-}C({=}O)}}{-}\right]^{+} \quad \text{(i)}$$

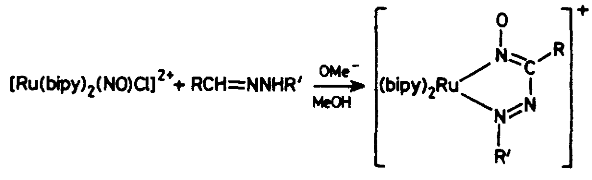
isolated and characterised using chemical, spectroscopic, and electrochemical methods. Two previous accounts on ruthenium arylazo-oximates exist.[2] Of relevance to the present work is the formation of the arylazo-oximate ring (1) by the reaction[2a] of $[\mathrm{Ru(NO)(NO_2)_4(OH)}]^{2-}$ with benzaldehyde phenylhydrazone. However, no pure complex could be isolated from this reaction.



(1)

Results and Discussion

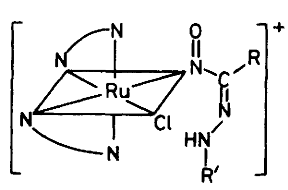
Synthesis and Characterisation of Complexes.—The four alkylidenearylhydrazones used were RCH=NNHR′ (R = R′ = Ph; R = Ph, R′ = C_6H_4Me-*p*; R = C_6H_4Me-*p*, R′ = Ph; R = Me, R′ = Ph). The reactions of $[\mathrm{Ru(bipy)_2(NO)Cl}]^{2+}$ with the first three hydrazones (the remaining hydrazone behaves differently, see below) proceed smoothly in methanol in the presence of NaOMe at room temperature [equation (ii)]. The cationic complex $[\mathrm{Ru(bipy)_2(A)}]^{+}$ (2) is isolated as the perchlorate monohydrate in good yield (A = arylazo-oximate anion). Specific arylazo-oximates are A^1, R = R′ = Ph; A^2, R = Ph, R′ = C_6H_4Me-*p*; A^3, R = C_6H_4Me-*p*, R′ = Ph; and A^4, R = Me, R′ = Ph (Table 1).



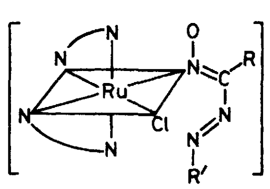
(2)

(ii)

The reaction (ii) becomes very slow or does not proceed at all in the absence of NaOMe. It is believed that OMe$^-$ abstracts a proton from the hydrazone producing the active nucleophile RC=NNHR′$^-$ which adds to the $[\mathrm{Ru(NO)}]^{3+}$ fragment. The initially formed *C*-nitroso-moiety (3) affords the conjugated azo-oxime species (4) *via* proton loss and electron reorganisation. The nucleophilic displacement of the *cis* halide by the terminal azo-nitrogen completes chelation, yielding (2). The crucial requirement in this scheme is the acidity of the C–H bond. That this bond in alkylidenearylhyrazones is acidic enough to couple with electrophiles in



(3)



(4)

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† Part 8 is ref. 28.

Table 1. Analytical data (%) for the complexes *

	Compound	Formula	C	H	N	Cl
(2a)	$[Ru(bipy)_2(A^1)][ClO_4]\cdot H_2O$	$C_{33}H_{28}ClN_7O_6Ru$	53.0 (53.2)	3.7 (3.8)	13.5 (13.2)	5.0 (4.8)
(2b)	$[Ru(bipy)_2(A^2)][ClO_4]\cdot H_2O$	$C_{34}H_{30}ClN_7O_6Ru$	54.4 (53.8)	3.8 (4.0)	12.9 (12.9)	4.7 (4.7)
(2c)	$[Ru(bipy)_2(A^3)][ClO_4]\cdot H_2O$	$C_{34}H_{30}ClN_7O_6Ru$	53.9 (53.8)	4.1 (4.0)	13.2 (12.9)	5.2 (4.7)
(2d)	$[Ru(bipy)_2(A^4)][ClO_4]\cdot H_2O$	$C_{28}H_{26}ClN_7O_6Ru$	49.4 (49.2)	3.6 (3.8)	13.9 (14.4)	5.5 (5.2)
(5b)	$[Ru(bipy)_2(HA^2)][ClO_4]_2\cdot H_2O$	$C_{34}H_{31}Cl_2N_7O_{10}Ru$	48.1 (47.5)	4.0 (3.6)	11.8 (11.4)	7.6 (8.3)
(5c)	$[Ru(bipy)_2(HA^3)][ClO_4]_2\cdot H_2O$	$C_{34}H_{31}Cl_2N_7O_{10}Ru$	47.3 (47.5)	3.6 (3.6)	10.8 (11.4)	8.1 (8.3)

* Calculated values are given in parentheses.

Table 2. Spectral and conductivity data of $[Ru(bipy)_2(A)][ClO_4]\cdot H_2O$ (2) and $[Ru(bipy)_2(HA)][ClO_4]_2\cdot H_2O$ (5)

	I.r. data [a] (cm^{-1})			
Compound	$\nu(C{=}N) + \nu(C{=}C)$	$\nu(NO)$	Λ_M [b]/Ω^{-1} cm^2 mol^{-1}	U.v.–visible spectral data [c] λ/nm (ε/dm^3 mol^{-1} cm^{-1})
(2a) [d]	1 600	1 235	175	448 (sh) (12 600), 404 (16 300), 282 (56 700), 252 (sh), 244 (30 000), 220 (31 700)
(2b)	1 600	1 235	170	448 (sh) (12 300), 406 (16 700), 284 (54 700), 252 (sh), 244 (30 000), 220 (32 400)
(2c)	1 600	1 235	160	448 (sh) (13 100), 408 (16 300), 284 (59 300), 252 (sh), 244 (30 800), 220 (33 700)
(2d) [e]	1 600	1 235	140	448 (10 800), 394 (17 500), 284 (44 100), 252 (sh), 244 (27 300)
(5b)	1 595	1 240	280	456 (11 800), 374 (13 100), 252 (br) (43 800),[f] 222 (58 000)
(5c)	1 595	1 240	285	456 (12 400), 360 (sh), 252 (br) (46 700),[f] 222 (57 500)

[a] KBr disc, 4 000—400 cm^{-1}: $\nu(C{=}N) + \nu(C{=}C)$, strong and sharp; $\nu(NO)$, very strong and broad. [b] Molar conductivity in MeCN at 298 K. [c] Spectral data of (2) and (5) were recorded in MeCN and 0.2 mol dm^{-3} $HClO_4$–MeCN respectively at 298 K; sh = shoulder, br = broad. [d] U.v.–visible spectral data in 0.2 mol dm^{-3} $HClO_4$–MeCN: 450 (16 200),360 (sh), 252 (br) (58 300) (see *f*), 224 (76 400). [e] U.v.–visible spectral data in 0.2 mol dm^{-3} $HClO_4$–MeCN: 440 (9 200), 360 (sh), 252 (br) (34 200) (see *f*), 223 (44 900). [f] Four bands, closely spaced.

basic media is reported [8] in the reaction with diazonium salts furnishing formazans. The proposed mechanism is similar to that considered for the nitrosation of $-COCH_2-$ species.[4,6a]

The methoxide ion is known [9] to add to the $[Ru(NO)]^{3+}$ moiety producing unstable $[Ru\{N(O)OMe\}]^{2+}$ species. However, this does not vitiate the basic features of the proposed mechanism. The presence of an equilibrium concentration of $[Ru(NO)]^{3+}$ would be sufficient. Alternatively or concurrently the carbanion can displace OMe^- from $[Ru\{N(O)OMe\}]^{2+}$ *via* nucleophilic attack at nitrogen producing (3).

Complexes of type (2) were also synthesized from NaA and *cis*-$[Ru(bipy)_2Cl_2]$ in methanol–water (1 : 1 v/v) [equation (iii)]. If instead of the sodium salt the free ligand is used, the protonated complex $[Ru(bipy)_2(HA)]^{2+}$ (5) is formed [equation (iv)]. This can also be obtained by adding acid ($HClO_4$) to (2) (see below). The complex $[Ru(bipy)_2(A^4)]^+$ could not be prepared by the nitrosation technique probably due to instability of the corresponding carbanion. It was obtained by the reaction (iii).

$$cis\text{-}[Ru(bipy)_2Cl_2] + NaA \longrightarrow (2) \qquad \text{(iii)}$$

$$cis\text{-}[Ru(bipy)_2Cl_2] + HA \longrightarrow (5) \qquad \text{(iv)}$$

All complexes prepared in the present work are isolated as yellow to brown perchlorate salts. Analytical data are given in Table 1. They are soluble in acetonitrile, pyridine, and methanol. In MeCN, $[Ru(bipy)_2(A)][ClO_4]\cdot H_2O$ and $[Ru(bipy)_2(HA)][ClO_4]_2\cdot H_2O$ behave as 1 : 1 and 1 : 2 electrolytes respectively (Table 2).

Spectra.—Both (2) and (5) are uniformly diamagnetic and display sharp ^1H n.m.r. signals in $[^2H_5]$pyridine {δ(Me): $[Ru(bipy)_2(A^2)]^+$, 2.10; $[Ru(bipy)_2(A^3)]^+$, 2.27; $[Ru(bipy)_2(A^4)]^+$, 2.80 p.p.m.}. The spectra of (2) and (5) are indistinguishable since in pyridine solution the conversion (5) ⟶ (4) occurs.

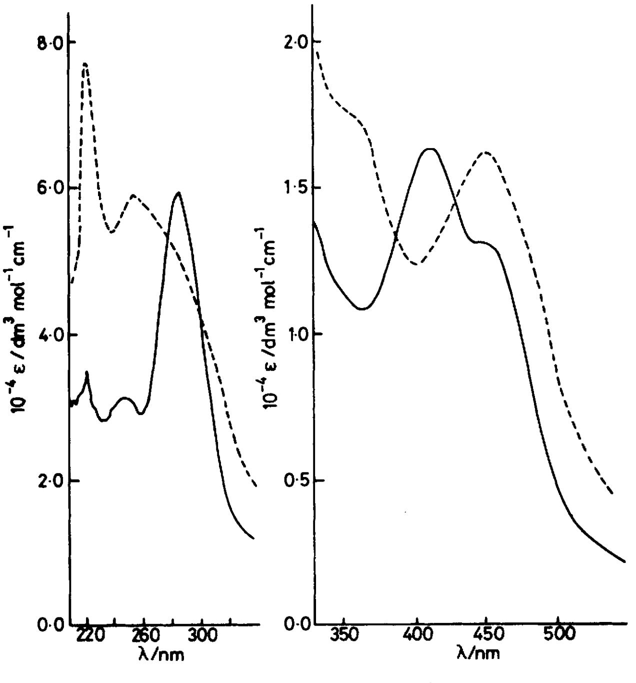

Figure 1. Electronic spectra of $[Ru(bipy)_2(A^3)]^+$ (——) in MeCN and $[Ru(bipy)_2(HA^1)]^{2+}$ (— — —) in 0.2 mol dm^{-3} $HClO_4$–MeCN

In the i.r. spectra, the characteristic [2a,10] NO stretching frequency of the five-membered arylazo-oximate chelate ring is observed near 1 240 cm^{-1} while $\nu(C{=}N) + \nu(C{=}C)$ occurs at *ca.* 1 600 cm^{-1} (Table 2). Bands due to unbound water (*ca.* 3 400 and *ca.* 1 630 cm^{-1}), ionic perchlorate (*ca.* 1 100 and *ca.* 620 cm^{-1}), and co-ordinated 2,2′-bipyridyl[11] are present in all complexes.

In acetonitrile, both (2) and (5) display several absorption bands in the visible and u.v. region (Table 2). An intense band occurs in (2) at *ca.* 400 nm associated with a shoulder near 450 nm; in (5) the corresponding band is at 450 nm (Figure 1). We assign the visible bands of (2) and (5) to metal $\longrightarrow$ ligand charge-transfer (m.l.c.t.) transitions.[4,12] The bands in the u.v. region are of intraligand ($\pi \longrightarrow \pi^*$) type.

Acidity of HA *in Free and Co-ordinated States.*—The oximate function in (2) can be protonated by $HClO_4$ affording (5) [equation (v)]. The reaction occurs in methanol as well as in dioxan–water (1 : 1). The latter solvent (1.0 mol dm^{-3} in

$$(2) + H^+ \longrightarrow (5) \qquad \text{(v)}$$

NaCl) was used for pH-metric determination of the proton dissociation constants of two complexes as well of the corresponding free ligands. The equilibria concerned are (vi) and (vii). The pK ($\pm$0.05) values are: $[Ru(bipy)_2(HA^1)]^{2+}$, 2.90;

$$(5) \overset{K}{\rightleftharpoons} (2) + H^+ \qquad \text{(vi)}$$

$$HA \overset{K}{\rightleftharpoons} A^- + H^+ \qquad \text{(vii)}$$

$[Ru(bipy)_2(HA^4)]^{2+}$, 3.00; HA^1, 9.85; HA^4, 10.10. As expected, α-(phenylazo)benzaldoxime (HA^1) is more acidic than α-(phenylazo)acetaldoxime (HA^4) both as a free ligand and in the complexed form. The metal bound oxime function is about 10^7 times more acidic than the free function. Whereas other examples of dramatic augmentation of oxime acidity on co-ordination exist in the literature,[1,13,14] the pK values of $[Ru(bipy)_2(HA)]^{2+}$ are exceptionally low among oxime complexes. This reflects the strong acceptor power of the $[Ru(bipy)_2]^{2+}$ moiety.

Electrochemistry.—The redox activities of (2) and (5) were examined at a platinum electrode in MeCN using cyclic voltammetry [all potentials are referenced to a saturated calomel electrode (s.c.e.)]. In (2), the Ru^{III}–Ru^{II} couple [equation (viii)] occurs near 0.8 V (Table 3). The anodic peak current (i_{pa}) has the expected * value but the cathodic peak

$$[Ru^{III}(bipy)_2(A)]^{2+} + e^- \rightleftharpoons [Ru^{II}(bipy)_2(A)]^+ \qquad \text{(viii)}$$

current (i_{pc}) is of diminished magnitude. The value of i_{pc}/i_{pa} increases with increasing scan rate (v) or decreasing the switching potential (E_λ) (Figure 2, Table 4). Therefore the oxidation of (2) is followed by a chemical reaction (ix) [electron transfer followed by fast chemical reactions (e.c.) mechanism[15]] where

$$[Ru^{III}(bipy)_2(A)]^{2+} \xrightarrow{k_f} \text{product(s)} \qquad \text{(ix)}$$

k_f is a pseudo-first-order rate constant. The k_f values for the various complexes are: $[Ru(bipy)_2(A^1)]^+$, 0.46; $[Ru(bipy)_2(A^2)]^+$, 0.43; $[Ru(bipy)_2(A^3)]^+$, 0.55 s^{-1}. In the case of $[Ru(bipy)_2(A^4)]^+$, the reaction (ix) was too fast for electrochemical determination of k_f. The product of the reaction (ix) is a complex mixture which has not been characterised.

Table 3. Cyclic voltammetric data[a] for $[Ru(bipy)_2(A)]^+$ and $[Ru(bipy)_2(HA)]^{2+}$

Complex	Ru^{III}–Ru^{II} couple $E_{298}{}^0$/V	Ru^{III}–Ru^{II} couple ΔE_p/mV	Ligand reduction $-E_{298}{}^0$/V (ΔE_p/mV)
$[Ru(bipy)_2(A^1)]^+$	0.81	70	1.26 (80), 1.56[b]
$[Ru(bipy)_2(A^2)]^+$	0.77	75	1.27 (140), 1.58[b]
$[Ru(bipy)_2(A^3)]^+$	0.77	70	1.22 (155)
$[Ru(bipy)_2(A^4)]^+$	0.75[c]	90	1.26 (100)
$[Ru(bipy)_2(HA^1)]^{2+}$	1.02	98	1.09,[b] 1.20 (120), 1.55[b]
$[Ru(bipy)_2(HA^2)]^{2+}$	1.01	115	1.10,[b] 1.23 (115), 1.55[b]
$[Ru(bipy)_2(HA^3)]^{2+}$	0.98	100	1.08,[b] 1.22 (115)
$[Ru(bipy)_2(HA^4)]^{2+}$	0.98[c]	100	*d*

[a] Cyclic voltammetry of the deprotonated and protonated species was carried out in MeCN and 0.2 mol dm^{-3} $HClO_4$–MeCN respectively at 298 K using 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ as a supporting electrolyte. The reported data correspond to scan rate v = 50 mV s^{-1}. [b] Cathodic peak potential with no anodic counterpart. [c] One more cathodic response (unknown origin) with diminished height was observed in the region 0.3—0.5 V. [d] Not studied.

Table 4. Evaluation of pseudo-first-order rate constant (k_f) of $[Ru(bipy)_2(A^1)]^+$ at 298 K in MeCN

v/mV s^{-1}	i_{pc}/i_{pa}	$k_f t$	t */s	E_λ/V	$E_{298}{}^0$/V	k_f/s^{-1}
200	0.47	1.14	2.46	1.30	0.81	0.46
200	0.58	0.69	1.48	1.10	0.81	0.47
300	0.56	0.75	1.64	1.30	0.81	0.46
300	0.67	0.46	0.98	1.10	0.81	0.47
400	0.62	0.57	1.23	1.30	0.81	0.46

* Sweep time (s) from the formal potential ($E_{298}{}^0$) to the switching potential (E_λ).

At scan rates where both anodic and cathodic peaks are observable, the peak-to-peak separation, ΔE_p, lies in the range 70—80 mV (Table 3). The electron-transfer process (viii) is thus quasi-reversible and the formal potential, $E_{298}{}^0$, is calculated as the average of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials (Table 3). Since an e.c. mechanism is operative, peak potentials would depend on the ratio k_f/v. However, for small values of this ratio (as in the present case) the effect is slight and $E_{298}{}^0$ can be set equal to the average of the peak potentials.[15]

For (5), the Ru^{III}–Ru^{II} couple in equation (x) occurs near 1.0 V (Table 3, Figure 3). Since addition of a proton makes electron removal thermodynamically more difficult,[4,13,16] the higher $E_{298}{}^0$ of couple (x) compared to that of couple (viii) is

$$[Ru^{III}(bipy)_2(HA)]^{3+} + e^- \rightleftharpoons [Ru^{II}(bipy)_2(HA)]^{2+} \qquad \text{(x)}$$

understandable. Here the oxidised complex is stable on the cyclic voltammetric time-scale (i_{pc}/i_{pa} *ca.* 1.0). The conversion (2) $\longrightarrow$ (5) could be followed electrochemically. Thus on successive addition of $HClO_4$ to an acetonitrile solution of (2) the response due to couple (viii) is progressively replaced by the response of couple (x). The latter response alone remains when the mol ratio (2) : $HClO_4$ becomes 1 : 1 (Figure 3). The

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* In our experimental set-up, an authentic Ru(III)–Ru(II) couple, *e.g.* $[Ru^{III}(bipy)_3]^{3+}$–$[Ru^{II}(bipy)_3]^{2+}$ has i_{pa} of 45 μA at v = 50 mV s^{-1} and 1.0 × 10^{-3} mol dm^{-3} solute concentration. In the present complexes i_{pa} values were 43—45 μA under the same conditions. Attempted coulometric oxidation of (2) at 1.0 V led to continuous coulomb accumulation due to unidentified reactions probably related to the decomposition of the oxidised complex (see text).

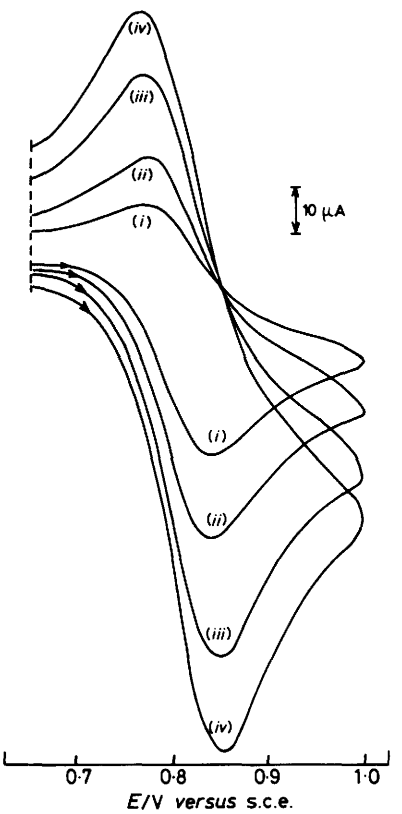

Figure 2. Cyclic voltammetric response of $[Ru(bipy)_2(A^1)]^+$ (1.0×10^{-3} mol dm^{-3}) in MeCN at scan rates of (*i*) 50, (*ii*) 100, (*iii*) 200, and (*iv*) 300 mV s^{-1}

hydroxyiminoketone complexes described elsewhere[4] behave similarly.

Both (2) and (5) display more than one response at potentials below −1.0 V (Table 3). These arise from ligand reduction.[2a,17-19]

Conclusions

We have demonstrated that $[Ru(bipy)_2(NO)Cl]^{2+}$ adds to alkylidenearylhydrazones giving $[Ru(bipy)_2(A)]^+$ which can be protonated to $[Ru(bipy)_2(HA)]^{2+}$. There is a 10^7-fold increase in the acidity of HA on co-ordination. Using the nitrosation reaction it should be possible to attach the $[Ru(bipy)_2]^{2+}$ chromophore to complex molecules having an aldehyde function *via* hydrazones. Such attachment could be of interest in biochemical problems.[20,21] Only two other groups of complexes having bidentate azo-ligands, 2-(arylazo)phenols[21] and 2-(arylazo)pyridines,[18] bound to $[Ru(bipy)_2]^{2+}$ are known. In (2) and (5) the co-ordination sphere is RuN_6. The $E_{298}{}^0$ values in MeCN of some other complexes of $[Ru(bipy)_2]^{2+}$ having the same sphere are: $[Ru(bipy)_3]^{2+}$, 1.29 V;[22] $[Ru(bipy)_2L]^{2+}$, [L = 2-(phenylazo)pyridine], 1.60 V;[18] $[Ru(bipy)_2(en)]^{2+}$ (en = ethylenediamine), 0.96 V;[22] $[Ru(bipy)_2\{C_6H_4(=NH)_2\text{-}1,2\}]^{2+}$, 1.68 V.[23] In the Ru^{III}–Ru^{II} couple, electron transfer occurs from the t_2 orbital which is stabilised by $M \longrightarrow L$ π interaction. In (2) and (5) this interaction appears to be relatively weak leading to $E_{298}{}^0$ values close to that of $[Ru(bipy)_2(en)]^{2+}$. The reaction of $RuCl_3$ with HA affords[2a] low-spin ($S = \frac{1}{2}$) $[Ru^{III}Cl_2(HA)(A)]$ in which the Ru^{III}–Ru^{II} couple occurs at *ca.* 0.5 V. On comparing with (2) and (5), it emerges that in arylazo-oximates of ruthenium, the +3 state is stabilised when halide is present as companion ligand while the +2 state dominates on co-ordination of bipy.

Experimental

Starting Materials.—Published methods[24,25] were used to prepare $[Ru(bipy)_2(NO)Cl][ClO_4]_2$ and *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$. Alkylidenearylhydrazones and arylazo-oximes were prepared by literature methods.[26,27] Electrochemically pure MeCN and $[NEt_4][ClO_4]$ were prepared as before.[2-4] For protonation experiments, a standard perchloric acid solution (0.2 mol dm^{-3} in MeCN) was used.

Physical Measurements.—U.v.–visible, i.r., and ^1H n.m.r. spectra were recorded using Pye-Unicam SP8-150, Beckman IR-20A, and Varian T-60A spectrometers respectively. Solution electrical conductivity was measured using a Philips PR 9500 bridge. Electrochemical measurements were carried out using a PAR 370-4 electrochemistry system as before;[2-4] a planar Beckman model 39273 platinum inlay working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode were used.[28] Electrochemical data were generally obtained at 298 K and are uncorrected for junction potentials.

The determination of pK was carried out at 298 K under a nitrogen atmosphere in dioxan-water (1 : 1) (ionic strength of the solution maintained at 1.0 mol dm^{-3} in NaCl) using a Systronics (India) 335 model pH-meter (accurate to ±0.01 pH unit) along with a glass electrode and s.c.e. For pK determination of the reaction (vi), $[Ru(bipy)_2(A)]^+$ (*ca.* 0.005 mol dm^{-3}) was titrated with standard hydrochloric acid (*ca.* 0.1 mol dm^{-3}). In the case of reaction (vii), HA (*ca.* 0.01 mol dm^{-3}) was titrated with standard sodium hydroxide (*ca.* 0.1 mol dm^{-3}). The usual equations[29] were used to calculate the pK value from the titration data.

Synthesis of Compounds.—*(Arylazo-oximato)bis(2,2′-bipyridyl)ruthenium*(II) *perchlorate monohydrate*, $[Ru(bipy)_2(A)][ClO_4]\cdot H_2O$. *Method* I. *From* $[Ru(bipy)_2(NO)Cl]^{2+}$ *and alkylidenearylhydrazones.* The complexes were prepared by nitrosation of RCH=NNHR′ using a general procedure. Details are given below for the preparation of $[Ru(bipy)_2(A^1)][ClO_4]\cdot H_2O$.

To a solution of 100 mg (0.15 mmol) of $[Ru(bipy)_2(NO)Cl][ClO_4]_2$ in methanol (10 cm^3) was added PhCH=NNHPh (80 mg, 0.41 mmol) and sodium methoxide (20 mg, 0.37 mmol). An immediate red colouration developed. The solution was stirred magnetically for 2 h. The solution colour changed from red to yellow-brown. The solution was then filtered and to the filtrate concentrated aqueous sodium perchlorate solution (*ca.* 5 cm^3) was added followed by the addition of water (20 cm^3). It was then kept at 273 K for 1 h. The precipitated complex was filtered off, washed with ice-cold water and finally with diethyl ether. The compound was dried *in vacuo* over P_4O_{10}. The crude product was then chromatographed on an alumina column (20 × 1 cm) in benzene solvent. The brown band of $[Ru(bipy)_2(A^1)][ClO_4]\cdot H_2O$ was eluted using benzene–acetonitrile (1 : 1 v/v) as the eluant. Slow evaporation of the eluate gave the desired product. Yield, 65 mg (60%). $[Ru(bipy)_2(A^2)][ClO_4]\cdot H_2O$ and $[Ru(bipy)_2(A^3)][ClO_4]\cdot H_2O$ were prepared similarly and the respective yields were 75 mg (65%) and 70 mg (60%).

Method II. *From* cis-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ *and* NaA. The complexes were prepared using a general procedure. Details for the preparation of $[Ru(bipy)_2(A^4)][ClO_4]\cdot H_2O$ are given below.

To $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (100 mg, 0.20 mmol) in methanol–

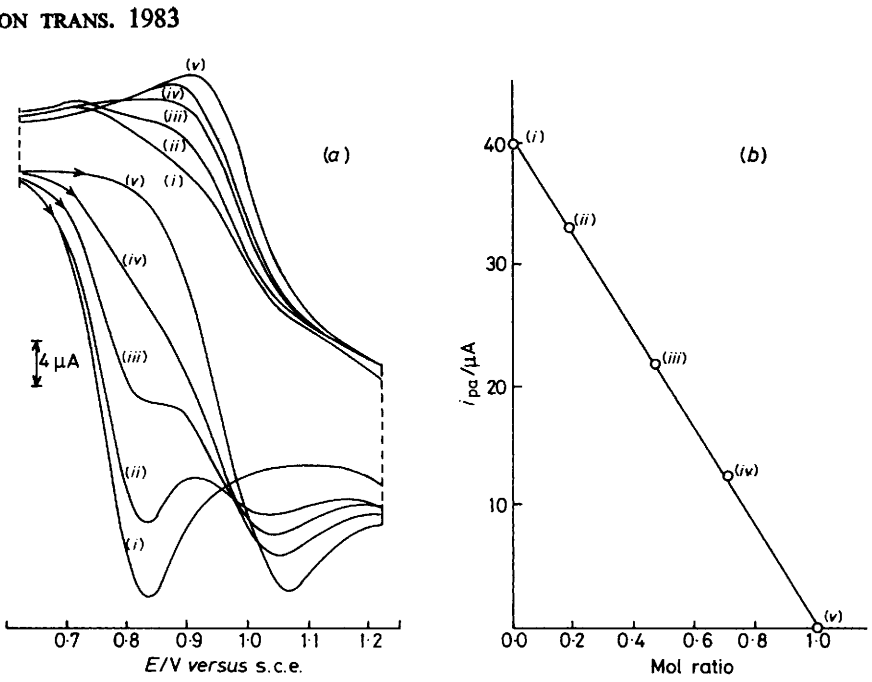

Figure 3. (*a*) Cyclic voltammograms and (*b*) anodic peak currents of $[Ru(bipy)_2(A^2)]^+$ at $[HClO_4]$: [Ru] mol ratios of (*i*) 0.0 : 1, (*ii*) 0.18 : 1, (*iii*) 0.46 : 1, (*iv*) 0.75 : 1, and (*v*) 1.00 : 1

water (1 : 1 v/v, 20 cm^3) was added a solution of α-(phenylazo)-acetaldoxime (HA^4; 40 mg, 0.25 mmol) in aqueous sodium hydroxide (1.0 mol dm^{-3}, 5 cm^3). The mixture was heated to reflux for 2 h. The solution changed from violet to brown; it was then cooled and filtered. To the filtrate concentrated aqueous sodium perchlorate solution (*ca.* 5 cm^3) was added followed by the addition of water (20 cm^3). The mixture was kept at 273 K for 1 h. The precipitated complex was filtered off and was washed thoroughly with ice-cold water. The air-dried product was recrystallised from methanol–water (1 : 1) containing a trace amount of sodium perchlorate. Yield, 125 mg (90%). $[Ru(bipy)_2(A^1)][ClO_4]\cdot H_2O$, $[Ru(bipy)_2(A^2)][ClO_4]\cdot H_2O$, and $[Ru(bipy)_2(A^3)][ClO_4]\cdot H_2O$ were prepared similarly. The yields were in the range 60—70%.

(*Arylazo-oxime*)*bis*(2,2′-*bipyridyl*)*ruthenium*(II) *diperchlorate monohydrate*, $[Ru(bipy)_2(HA)][ClO_4]_2\cdot H_2O$. Pure salts were isolated for the ligands HA^2 and HA^3. In other cases a mixture of the protonated and deprotonated species resulted. Both $[Ru(bipy)_2(HA^2)][ClO_4]_2\cdot H_2O$ and $[Ru(bipy)_2(HA^3)][ClO_4]_2\cdot H_2O$ were prepared using a general procedure with *ca.* 70% yields. Details are given below.

To a solution of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (100 mg, 0.20 mmol) in methanol–water (1 : 1 v/v, 20 cm^3) was added 60 mg (0.25 mmol) of α-(*p*-tolylazo)benzaldoxime (HA^2) or α-(phenylazo)-*p*-tolualdoxime (HA^3). The mixture was heated to reflux for 2 h. The colour of the solution changed from violet to yellow-brown. The resulting solution was cooled and filtered. To the filtrate a concentrated aqueous solution of sodium perchlorate containing perchloric acid (20 : 1 v/v) was added. The precipitated complex was filtered off and washed first with ice-cold water then with benzene and finally with diethyl ether. The yellow-brown complex was dried under vacuum over P_4O_{10}. Yield, 120 mg (70%).

Conversion of $[Ru(bipy)_2(A)][ClO_4]\cdot H_2O$ *to* $[Ru(bipy)_2(HA)][ClO_4]_2\cdot H_2O$ *by* $HClO_4$.—$[Ru(bipy)_2(A)][ClO_4]\cdot H_2O$ (50 mg; A = A^2 or A^3) was dissolved in MeOH (20 cm^3). To this solution a concentrated aqueous solution of sodium perchlorate containing perchloric acid (10 : 1 v/v, 5 cm^3) was added followed by an addition of water (20 cm^3). The complex thus precipitated was filtered off, washed with ice-cold water and dried *in vacuo* over P_4O_{10}. Yield *ca.* 80%.

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