Synthesis, Characterisation and Variable-temperature Nuclear Magnetic Resonance of Bis(bipyridine)ruthenium Complexes containing Dihydrazone Ligands *

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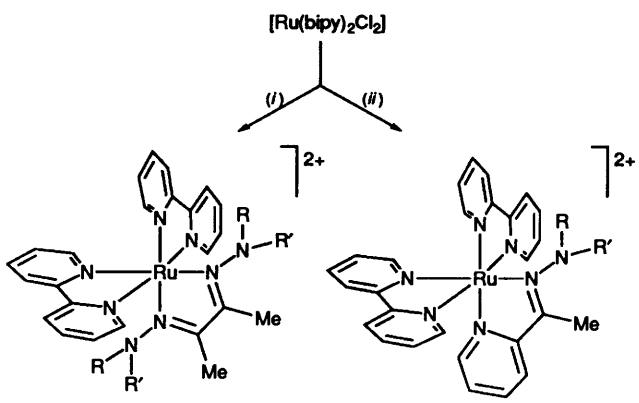
A series of dihydrazone and substituted dihydrazone derivatives of biacetyl and of hydrazone and phenylhydrazone derivatives of 2-acetylpyridine bind to $[Ru(bipy)_2Cl_2]$ to give $[Ru(bipy)_2(L–L)][PF_6]_2$ complexes {bipy = 2,2'-bipyridine; L–L = biacetyl di(phenylhydrazone) **1a**, biacetyl di[methyl(phenyl)hydrazone] **1b**, biacetyl di(*o*-tolylhydrazone) **1c**, biacetyl di(dimethylhydrazone) **1d**, biacetyl dihydrazone **1e**, biacetyl di(benzaldehyde azine) **1f**, 2-acetylpyridine phenylhydrazone **1g**, or 2-acetylpyridine hydrazone **1h**}. The structures of all complexes have been determined using IR, UV/VIS, NMR and microanalysis. The proton NMR spectra of **1a–1c** show an unusual dependence on probe temperature with broadened aromatic resonances, sharpening at both high and low temperature in the case of **1b** and **1c**. No emission was observed for complexes with two hydrazone moieties, whereas it was observed for **1g** and **1h** with one hydrazone. The molecular structure of **1a** has been determined and shows a hydrazone phenyl group lying over each of the bipyridyl rings: space group $C2/c$, $a = 25.895(3)$, $b = 10.505(1)$, $c = 17.431(2)$ Å, $\beta = 106.03(2)°$ and $Z = 4$.

A considerable amount of research has been carried out on ruthenium(II) complexes containing 2,2'-bipyridine (bipy) or 1,10-phenanthroline ligands, principally because $[Ru(bipy)_3]^{2+}$ has been recognised as a potential photocatalyst.[1–3] However, $[Ru(bipy)_3]^{2+}$ is not the most suitable photocatalyst as population of the metal-centred triplet state leads to photodecomposition of the complex and because of its rather narrow absorption band at 452 nm only a small part of the solar spectrum is utilised.[4,5] By changing the ligand systems around the ruthenium(II) centre it is possible to alter the ground- and excited-state properties of the complexes and also the energies of the absorption and emission bands.[6] The use of mixed-ligand complexes is part of on-going research to find more useful photocatalysts, which are photostable and have more suitable absorption/emission properties than those of the parent $[Ru(bipy)_3]^{2+}$.[6]

In this contribution the preparation and characterisation of the first complexes of $Ru(bipy)_2$ with both dihydrazones and substituted dihydrazones of biacetyl and the phenylhydrazone and hydrazone of 2-acetylpyridine are described. A considerable amount of work has been published relating to the use of dihydrazones as ligands for first-row transition-metal complexes of biacetyl hydrazone[7] and palladium complexes of biacetyl diphenylhydrazone[8] and biacetyl di(methylphenylhydrazone)[9] but to date no ruthenium complexes have been reported.



	R	R'
1a	H	Ph
1b	Me	Ph
1c	H	C_6H_4Me-*o*
1d	Me	Me
1e	H	H
1f	R/R' = CHPh	

	R	R'
1g	H	Ph
1h	H	H

Scheme 1 Preparation of complexes **1a–1h**. (*i*) Ligands **Ia–If**; (*ii*) **Ig** or **Ih**

Results and Discussion

Synthesis.—The ligands **Ia–Ih** (see Scheme 1) were prepared using standard literature methods with only slight modifications.[10–14] The dihydrazone **Ie** and substituted dihydrazones **Ia–Id** were prepared by treating 2 equivalents of the corresponding hydrazine with 1 equivalent of biacetyl. For the hydrazones **Ie** and **Ih** no azines were detected resulting from attack of the terminal amino group on unreacted carbonyl groups. On reflux of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ with 1.2 molar equivalents of each of the ligands **Ia–Ih** in aqueous ethanol the corresponding $[Ru(bipy)_2(L–L)]^{2+}$ complexes **1a–1h** were produced according to Scheme 1. After complexation of **Ie** to form **1e** the terminal amino groups of the hydrazones in **1e** were treated with benzaldehyde to give the complex **1f** which was prepared independently from the azine **If** resulting from the reaction of **Ie** and benzaldehyde prior to complexation. This

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Fractional atomic coordinates for compound **1a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0	0.779 60(4)	0.750 00	C(35)	−0.089 0(2)	0.816 0(6)	0.925 9(3)
N(1)	0.041 2(1)	0.930 7(3)	0.806 8(1)	C(36)	−0.053 9(2)	0.834 6(4)	0.881 3(2)
N(2)	0.088 5(1)	0.923 5(3)	0.873 9(2)	P	0.594 61(5)	0.742 23(12)	0.598 40(7)
N(3)	−0.053 3(1)	0.761 7(3)	0.818 0(2)	F(1)	0.561 8(1)	0.639 0(3)	0.631 0(2)
N(4)	−0.050 2(1)	0.634 9(3)	0.690 6(2)	F(2)	0.555 0(2)	0.846 5(4)	0.609 3(4)
C(1)	0.024 8(1)	1.044 7(3)	0.783 9(2)	F(3)	0.561 6(2)	0.718 2(5)	0.510 8(2)
C(2)	0.050 3(2)	1.166 3(4)	0.819 1(2)	F(4)	0.631 4(2)	0.767 1(5)	0.685 8(2)
C(11)	0.136 7(1)	0.894 6(3)	0.851 4(2)	F(5)	0.636 1(2)	0.638 0(4)	0.589 6(4)
C(12)	0.148 1(1)	0.953 3(4)	0.787 6(2)	F(6)	0.629 0(1)	0.845 9(4)	0.570 0(2)
C(13)	0.196 2(2)	0.930 5(6)	0.771 5(3)	F(11)	0.538 6(20)	0.834 4(59)	0.542 8(31)
C(14)	0.232 5(2)	0.847 7(7)	0.818 6(4)	F(21)	0.593 5(23)	0.816 0(45)	0.673 6(28)
C(15)	0.221 3(2)	0.788 7(6)	0.882 9(4)	F(31)	0.638 1(17)	0.653 0(47)	0.643 4(30)
C(16)	0.173 2(2)	0.812 4(4)	0.899 2(2)	F(41)	0.594 4(24)	0.640 5(51)	0.535 0(33)
C(22)	−0.087 2(1)	0.596 3(3)	0.724 8(2)	C(1a)	0.269 1(3)	0.332 9(6)	0.067 4(4)
C(23)	−0.122 6(2)	0.497 9(4)	0.691 3(3)	C(1b)	0.259 8(3)	0.229 8(6)	0.112 3(4)
C(24)	−0.119 0(2)	0.442 0(4)	0.623 4(4)	C(1c)	0.240 1(3)	0.115 7(6)	0.074 5(4)
C(25)	−0.079 8(2)	0.480 0(4)	0.587 4(3)	C(1d)	0.229 7(3)	0.104 6(6)	−0.008 1(4)
C(26)	−0.045 8(2)	0.577 7(4)	0.623 4(2)	C(1e)	0.239 0(3)	0.207 7(6)	−0.053 0(4)
C(32)	−0.089 2(1)	0.666 2(4)	0.796 4(2)	C(1f)	0.258 7(3)	0.321 9(6)	−0.015 2(4)
C(33)	−0.125 3(2)	0.641 8(5)	0.840 9(3)	C(1g)	0.276 1(9)	0.432 8(15)	−0.054 7(12)
C(34)	−0.125 6(2)	0.714 8(6)	0.905 1(4)				

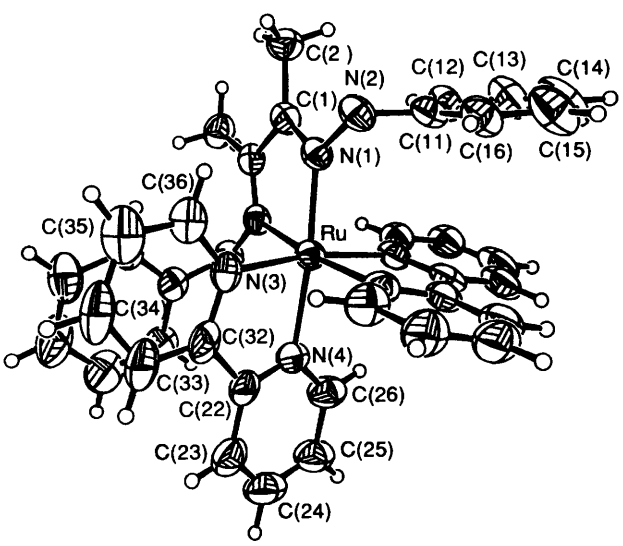


Fig. 1 Crystal structure of the cation of complex **1a**

shows that the reactivity of the amino groups of the ligands remains relatively unchanged and provides the possibility of binding these complexes to other moieties through these groups.

Reaction progress was monitored by cation-exchange HPLC using an on-line photodiode-array detector. The complexes were found to have absorption maxima in the range 420–455 nm, indicative of the six co-ordination sites of the ruthenium atom being filled by nitrogen σ donors. After completion of the reaction, the solvent was removed and the residue reconstituted into distilled water. Excess of ligand was removed by extraction into diethyl ether. Dropwise addition of the aqueous solution of complex to an aqueous solution of ammonium hexafluorophosphate resulted in precipitation of $[Ru(bipy)_2(L\text{–}L)][PF_6]_2$ **1a**–**1h**. All the complexes gave satisfactory elemental analysis. They were further characterised using spectroscopic techniques (see below).

Crystal Structure of Complex **1a**.—The crystal structure of the cation is illustrated in Fig. 1. Fractional atomic coordinates are given in Table 1, relevant bond lengths and angles in Tables 2 and 3 respectively.

The complex exhibits pseudo-octahedral geometry with the ruthenium ion bound to two bipyridyl rings orientated in a *cis* configuration along with biacetyl di(phenylhydrazone) co-ordinated by the N(1) nitrogens. The complex is symmetric with a two-fold axis bisecting the biacetyl ligand. The phenyl rings are located over a bipyridyl ring which is of importance for understanding the proton NMR spectra obtained for this and other compounds (see below).

The bond lengths for the biacetyl di(phenylhydrazone) to ruthenium are significantly shorter, Ru–N(1) 2.013(3) Å, compared to the Ru–N bond lengths observed for the bipy ligands, Ru–N(3) 2.060(3) and Ru–N(4) 2.081(3) Å. The latter are in good agreement with the average value of 2.056 Å found for $[Ru(bipy)_3][PF_6]_2$ [15] and similar bis(bipyridyl)ruthenium complexes.[16–21] The Ru–N distances to the dihydrazone ligand are considerably shorter than in similar compounds, *e.g.* shorter than for the negatively charged triazolato ring.[18–20] This suggests that the ligand has strong σ-donor properties and is consistent with the observed photostability of the complexes. The bite angle of the biacetyl di(phenylhydrazone) ligand N(1)–Ru–N(1) is 75.9(2)° compared to a bond angle of 78.1(1)° for the bipyridine ligand, which is normal for this type of compound.

NMR Studies.—Proton NMR spectroscopy can be very useful for the structural determination of ruthenium polypyridyl complexes since very well defined spectra with high resolution are normally obtained. The spectrum of complex **1a** at room temperature in $(CD_3)_2CO$ or $(CD_3)_2SO$ gave the expected four resonances for each pyridyl ring, a non-primed set H^3, H^4, H^5, H^6 and a primed set $H^{3'}$, $H^{4'}$, $H^{5'}$ and $H^{6'}$, and were assigned unequivocally using the correlation spectroscopy (COSY) technique. The phenyl resonances occurred at δ 5.8 for the *ortho*-protons $H^{2''}$ and at δ 6.5 for the *meta*- and *para*-protons $H^{3''}$ and $H^{4''}$. The high-field resonances for the *o*-protons when compared to those of the free ligand (δ 7.3) show that these protons are particularly influenced by the shielding effect of bipyridyl ring currents. Similarly for **1b** both of the *o*-protons appear at δ 6.0 while for **1c** the *o*-proton is at δ 5.5. An upfield shift also occurs for the *N*-methyl groups, from δ 1.9 in complex **1d** to δ 2.7 for the free ligand. Negligible changes for the aromatic proton resonances of **1f** are observed on complexation. Some of the proton resonances of the free ligands **Ia**–**Ih** and their complexes **1a**–**1h** are given in Table 4.

Although the proton spectra obtained could be analysed in a

Table 2 Bond lengths (Å) for compound **1a**

Ru–N(1)	2.013(3)	Ru–N(3)	2.060(3)
Ru–N(4)	2.081(3)	N(1)–N(2)	1.444(3)
N(1)–C(1)	1.296(5)	N(2)–C(11)	1.439(5)
N(3)–C(32)	1.349(5)	N(3)–C(36)	1.347(5)
N(4)–C(22)	1.323(5)	N(4)–C(26)	1.350(5)
C(1)–C(2)	1.490(5)	C(1)–C(1)	1.487(6)
C(11)–C(12)	1.374(5)	C(11)–C(16)	1.378(5)
C(12)–C(13)	1.371(6)	C(13)–C(14)	1.374(8)
C(14)–C(15)	1.380(9)	C(15)–C(16)	1.376(7)
C(22)–C(23)	1.398(6)	C(22)–C(32)	1.461(6)
C(23)–C(24)	1.348(8)	C(24)–C(25)	1.390(8)
C(25)–C(26)	1.385(6)	C(32)–C(33)	1.393(6)
C(33)–C(34)	1.359(7)	C(34)–C(35)	1.403(8)
C(35)–C(36)	1.363(6)	P–F(1)	1.577(3)
P–F(2)	1.547(4)	P–F(3)	1.550(3)
P–F(4)	1.579(4)	P–F(5)	1.577(4)
P–F(6)	1.571(3)	P–F(11)	1.79(5)
P–F(21)	1.53(4)	P–F(31)	1.51(4)
P–F(41)	1.53(5)	F(2)–F(11)	1.13(5)
F(2)–F(21)	1.32(5)	F(3)–F(11)	1.53(5)
F(3)–F(41)	1.17(6)	F(4)–F(21)	1.08(5)
F(4)–F(31)	1.44(5)	F(5)–F(31)	0.94(5)
F(5)–F(41)	1.23(6)	C(1a)–C(1b)	1.395(1)
C(1a)–C(1f)	1.395(1)	C(1b)–C(1c)	1.395(1)
C(1c)–C(1d)	1.395(1)	C(1d)–C(1e)	1.395(1)
C(1e)–C(1f)	1.395(1)	C(1e)–C(1e)	1.99(1)
C(1f)–C(1g)	1.485(9)	C(1f)–C(1f)	1.70(1)

Table 3 Bond angles (°) for compound **1a**

N(3)–Ru–N(1)	97.9(1)	N(4)–Ru–N(1)	173.7(1)
N(4)–Ru–N(3)	78.1(1)	N(2)–N(1)–Ru	124.9(2)
C(1)–N(1)–Ru	119.5(2)	C(1)–N(1)–N(2)	115.5(3)
N(1)–Ru–N(1)	75.9(2)	C(11)–N(2)–N(1)	113.4(3)
C(32)–N(3)–Ru	115.3(3)	C(36)–N(3)–Ru	125.5(3)
C(36)–N(3)–C(32)	119.2(4)	C(22)–N(4)–Ru	115.5(3)
C(26)–N(4)–Ru	124.4(3)	C(26)–N(4)–C(22)	120.0(3)
N(4)–Ru–N(4)	86.1(1)	C(2)–C(1)–N(1)	126.6(3)
C(12)–C(11)–N(2)	121.5(3)	C(16)–C(11)–N(2)	118.0(4)
C(16)–C(11)–C(12)	120.4(4)	C(13)–C(12)–C(11)	119.9(4)
C(14)–C(13)–C(12)	120.0(5)	C(15)–C(14)–C(13)	120.4(5)
C(16)–C(15)–C(14)	119.5(5)	C(15)–C(16)–C(11)	119.9(5)
C(23)–C(22)–N(4)	120.8(4)	C(32)–C(22)–N(4)	115.5(3)
C(32)–C(22)–C(23)	123.7(4)	C(24)–C(23)–C(22)	119.4(5)
C(25)–C(24)–C(23)	120.5(4)	C(26)–C(25)–C(24)	117.4(5)
C(25)–C(26)–N(4)	121.8(4)	C(22)–C(32)–N(3)	115.3(3)
C(33)–C(32)–N(3)	119.9(4)	C(33)–C(32)–C(22)	124.8(4)
C(34)–C(33)–C(32)	120.9(5)	C(35)–C(34)–C(33)	118.8(4)
C(36)–C(35)–C(34)	118.1(5)	C(35)–C(36)–N(3)	123.2(5)
F(2)–P–F(1)	90.1(2)	F(3)–P–F(1)	92.2(2)
F(3)–P–F(2)	91.9(3)	F(4)–P–F(1)	90.4(2)
F(4)–P–F(2)	90.5(3)	F(4)–P–F(3)	176.5(3)
F(5)–P–F(1)	90.4(2)	F(5)–P–F(2)	178.3(3)
F(5)–P–F(3)	89.8(3)	F(5)–P–F(4)	87.9(3)
F(6)–P–F(1)	177.3(2)	F(6)–P–F(2)	90.0(2)
F(6)–P–F(3)	90.5(2)	F(6)–P–F(4)	86.9(2)
F(6)–P–F(5)	89.4(2)	F(11)–P–F(1)	97(2)
F(11)–P–F(2)	39(2)	F(11)–P–F(3)	54(2)
F(11)–P–F(4)	128(2)	F(11)–P–F(5)	143(2)
F(11)–P–F(6)	84(2)	F(21)–P–F(1)	84(2)
F(21)–P–F(2)	51(2)	F(21)–P–F(3)	142(2)
F(21)–P–F(4)	40(2)	F(21)–P–F(5)	128(2)
F(21)–P–F(6)	94(2)	F(21)–P–F(11)	89(2)
F(31)–P–F(1)	78(2)	F(31)–P–F(2)	143(2)
F(31)–P–F(3)	123(2)	F(31)–P–F(4)	56(2)
F(31)–P–F(5)	35(2)	F(31)–P–F(6)	101(2)
F(31)–P–F(11)	174(3)	F(31)–P–F(21)	93(2)

satisfactory manner certain resonances appeared as broad ill defined peaks (see 293 K in Fig. 2). There have been a number of reports on the temperature dependence of NMR spectra of complexes containing an aromatic ring which is free to rotate.[14,22] Pertinent examples include the ^{1}H NMR spectra of $[Ru(p\text{-}MeC_6H_4N{=}CMe{-}CMe{=}NC_6H_4Me\text{-}p)_2Cl_2]$ where the aromatic group is free to rotate about the N–C bond,[14] and of $[Ru(bipy)_2(tbipy)][PF_6]_2$ (tbipy = 6-*p*-tolyl-2,2′-bipyridine) with a freely rotating tolyl ring.[22] It was therefore decided to investigate the broadening effect by variable-temperature NMR studies.

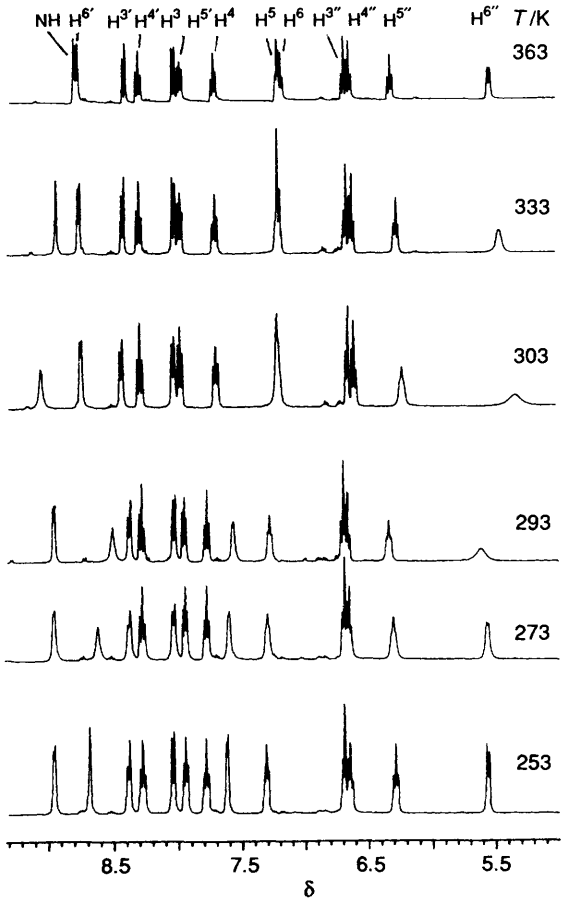


Fig. 2 Aromatic region of the ^{1}H NMR spectrum of complex **1c**. Solvent: $(CD_3)_2SO$ from 363 to 303 K; $(CD_3)_2CO$ from 293 to 253 K

These studies were carried out on complexes **1a**–**1c** in $(CD_3)_2CO$ for low-temperature and in $(CD_3)_2SO$ for high temperature experiments. Significant broadening of the phenyl resonances was observed for each of the complexes at various temperatures. In the case of **1a** when the temperature was raised from 293 to 363 K the NH signal disappeared without broadening of the aromatic signals. However on lowering the temperature to 193 K the phenyl *o*-proton peak broadened significantly (and to a lesser extent the *meta*/*para* resonances) while undergoing a small downfield shift. No change in the bipyridyl resonances was observed.

The introduction of a methyl group at the *ortho* position of the phenyl ring gives more striking broadening of signals. For the *o*-methylphenyl derivative **1c** a room-temperature spectrum reveals a single *o*-hydrogen resonance at δ 5.5 as a broad signal which sharpens with both increasing (see 363 K in Fig. 2) and decreasing temperature (see 253 K in Fig. 2). At both high and low temperature eight signals for the bipyridyl system (H^3, H^4, H^5, H^6 and $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{6'}$) and four for the tolyl group are observed.

The introduction of a methyl group on the amino nitrogen results in a broadening of bipyridyl resonances in particular the H^5 and H^6 and phenyl resonances. For the *N*-methyl-substituted complex **1b** almost all of the aromatic resonances are broadened at room temperature. The H^6 and H^5 resonances

Table 4 Selected chemical shifts (^{1}H) for ligands **la**–**lh** and complexes **1a**–**1h**

	δ (phenyl protons)							δ (bipy proton)							
Compound	H^2	H^3	H^4	H^5	H^6	$\delta(CH_3)$	$\delta(CH_3')$	H^6	H^5	H^4	H^3	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$
la	7.3	7.3	6.9	7.3	7.3	2.3									
1a	5.8	6.5	6.5	6.5	5.8	2.8		7.2	7.3	7.8	8.1	8.3	8.2	7.9	8.4
lb	7.0	7.3	6.9	7.3	7.0	2.2	3.2								
1b	6.0	6.6	6.6	6.6	6.0	2.9	3.0	7.0	7.2	7.8	8.1	8.3	8.2	7.9	8.9
lc		7.7	7.3	6.9	7.3	2.2	2.5								
1c		6.6	6.9	6.3	5.5	2.5	2.2	7.1	7.2	7.7	7.9	8.3	8.2	7.9	8.7
ld						1.9	2.7								
1d						2.7	1.9	7.7	7.3	8.0	8.7	8.2	7.8	8.3	8.9
le[a]						1.8									
1e[b]						2.5		7.4	7.4	8.0	8.7	8.2	7.8	8.3	8.8
lf	7.7	7.4	7.4	7.4	7.7	2.2									
1f	7.5	7.5	7.5	7.5	7.5	2.8		7.6	7.3	7.8	8.5	8.7	7.9	8.4	8.8

[a] $\delta(NH_2)$ 5.8. [b] $\delta(NH_2)$ 6.5.

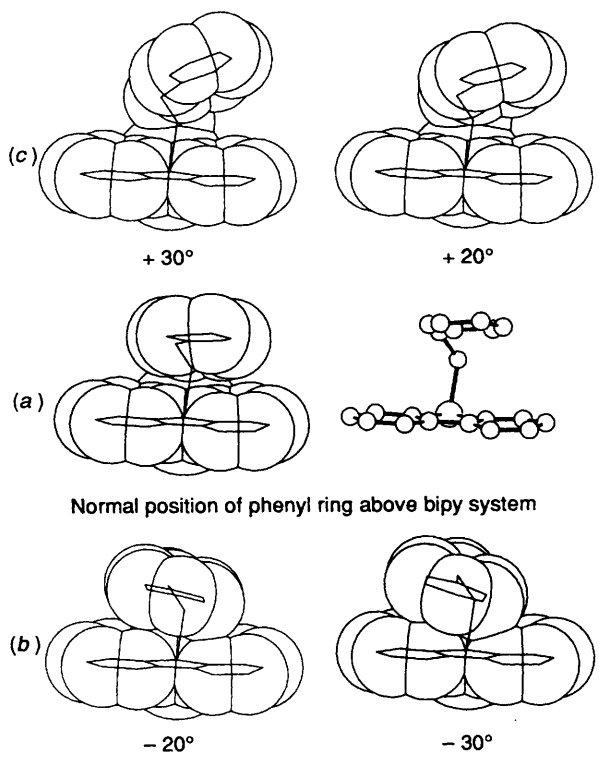


Fig. 3 Effect of various angles of rotation about the N–N bond for a phenyl ring over a bipy ring in complex **1a**

of the bipyridyl rings are broad and baseline respectively. On raising the temperature all aromatic signals sharpen and give the expected eight bipyridyl signals at 373 K. Also, reducing the temperature results in a sharpening of signals without an increase in either the number of signals or change in chemical shift.

The broadening of resonances for complexes **1a**–**1c** may be attributed to the exchange of the phenyl ring proton environments which would result from rotation about either the N–N or C–N bond. From examination of molecular models it is clear that rotation about the N–C bond is severely hindered on steric grounds (see Fig. 3). Rotation about the N–N bond is possible for ± 15° and leads to movement across the bipyridyl ring system. Further rotation results in removal of the favourable interactions between the phenyl and bipyridyl aromatic π systems. These limitations in molecular motion result in the phenyl moiety existing in a shallow potential well. Rapid (on the NMR time-scale) oscillation with increased temperature leads to sharpening of signals corresponding to the averaged proton

Table 5 Redox and spectroscopic properties of ruthenium(II) dihydrazone compounds[a]

		E/V *vs.* SCE	
Complex	Absorption λ/nm (log ε)	Oxidation waves	Ligand-based reductions
1a	450 (4.25)	1.6, 1.1	−1.1, −1.5, −1.8
1b	455 (4.23)	1.9, 1.3, 1.1	−1.0, −1.6, −1.9
1c	450 (4.24)	1.6, 1.1	−1.1, −1.6, −1.8
1d	450 (3.90)	1.3	−1.1, −1.5, −1.9
1e	420 (3.97)	1.4, 1.2	−1.3, −1.5, −1.7
1f	450 (4.04)	1.4	−0.9, −1.5, −1.8
1g[b]	455 (4.24)	1.6, 1.1, 0.9	−1.2, −1.5, −1.7
1h[c]	440 (4.28)	1.3	−1.3, −1.5, −1.7

[a] All measurements carried out in acetonitrile, except emission measurements at 77 K (ethanol). Background electrolyte for electrochemical experiments, 0.1 mol dm^{-3} lithium perchlorate. [b] Emission at λ 670 (293K) and 595 nm (77 K). [c] Emission at λ 660 (293 K) and 604 nm (77 K).

environment within this potential well. Even at high temperature the phenyl ring remains in this potential well since the *o*-protons maintain their chemical shift resulting from interaction with the bipyridyl π system. On lowering of temperature the slow exchange (relative to the NMR time-scale) of the phenyl proton environment again results in a sharp signal. In keeping with the suggestion that rotation about the N–N bond occurs (rather than about N–C), placing a methyl group onto the amino nitrogen does significantly affect the variable-temperature NMR spectra.

The suggestion of a phenyl ring lying close in space (< 3 Å) over a bipyridyl group is supported by a difference nuclear Overhauser effect (NOE) study on complex **1a**. On irradiation the *o*-hydrogens (signal at δ 5.8) show a 2.5% NOE to the $H^{6'}$ and a 1.8% NOE to the H^6 protons of the bipyridyl system in addition to a 4.0% NOE to the NH proton. Similarly, the *o*-methyl of **1c** gives small NOEs to $H^{6'}$, H^6 and H^5 of the bipyridyl moiety, the resonances of which experience greatest broadening.

Redox and Excited-state Properties.—The redox UV/VIS and emission data obtained for compounds **1a**–**1g** are summarised in Table 5. Except for **1e** the absorption maxima observed in the visible region are similar to those for $[Ru(bipy)_3]^{2+}$. Considering the energy of the absorption it is somewhat surprising that complexes **1a**–**1f** do not exhibit emission, even at low temperature in a range of solvents. However an emission was observed for **1g** and **1h** at room temperature. Often the lack of emission in ruthenium(II) polypyridyl complexes is related to an efficient population of the antibonding d–d orbital which results in photochemical decomposition. Even in these cases

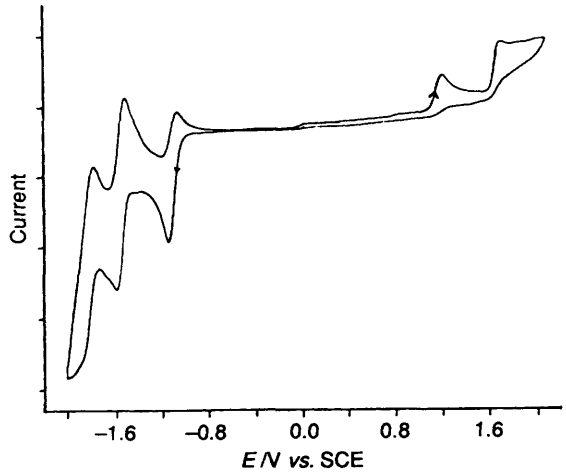


Fig. 4 Cyclic voltammogram of complex **1a** in 0.1 mol dm^{-3} NEt_4ClO_4 in acetonitrile

emission is observed at 77 K and the complexes are photolabile.[6] However **1a**–**1c** and **1f** are photostable upon irradiation with visible light in CH_2Cl_2 containing 0.05 mol dm^{-3} tetraethylammonium bromide so it is unlikely that the d–d orbital is populated. An alternative explanation for the absence of emission is that the dihydrazone ligands are directly involved in the excited-state processes and that population of a dihydrazone excited state leads only to radiationless processes. Evidence to support this assumption can be obtained from the magnitude of the ligand-based reduction potentials for these compounds. For compounds **1a**–**1f** the first ligand-based reduction is found between −1.1 and −1.2 V *vs.* saturated calomel electrode (SCE), about 100–200 mV less negative than for $[Ru(bipy)_3]^{2+}$ (see Table 5).[6] The free ligands do not show well defined electrochemistry, except that for **If** a reduction potential was observed at −1.5 V. These reduction potentials suggest that the dihydrazone ligands are better π-acceptor ligands than is bipy and as a consequence the lowest triplet metal-to-ligand charge-transfer (^{3}m.l.c.t.) level is most likely based on the dihydrazone ligands and not on bipy. Therefore the dihydrazone ligands are not just spectator ligands but are expected to control the excited-state processes. Preliminary resonance-Raman experiments carried out on these compounds confirm this interpretation.[23] Since the energy of the potentially emitting dihydrazone-based orbital is expected to be low it is necessary to consider the possibility resulting from the energy-gap law that the emission is very low. It is also possible that the emission falls outside the range measured (500–900 nm). Interestingly for compounds **1g** and **1h** a weak emission signal is observed at room temperature. At the same time the first ligand-based reduction of these two compounds is found at more negative potentials. This suggests that with the mixed pyridine–hydrazone ligands such as **Ig** and **Ih** the population of the bipy-based ^{3}m.l.c.t. level results in emission. The more negative reduction potential suggests a higher energy for the ^{3}m.l.c.t. level. This, when coupled with a reduced σ-donation ability of the ligands **If** and **Ih**, reduces the energy of the antibonding d–d level which leads to photodecomposition.

It is noteworthy that all complexes containing one hydrazone chain close to each bipyridyl ring system are photostable, whereas the other complexes decompose upon photolysis in CH_2Cl_2–0.05 mol dm^{-3} NEt_4Br. The presence of the phenyl rings close to the bipy rings might act further to stabilise these compounds (**1a**–**1c**).

Limited information could be obtained for the metal-based oxidation processes for these compounds. This is because most dihydrazone ligands show irreversible oxidations in the range 1.0–1.5 V, both as free ligands and when co-ordinated. An example of a typical cyclovoltammogram is given in Fig. 4. Reversible electrochemistry in this range was only obtained for compounds **1d**, **1f** and **1h**. The rather high oxidation potentials obtained are indicative of the presence of strong π-acceptor ligands.

Conclusion

The study of these hydrazone-containing compounds, having the same central N=C–C=N unit as polypyridyl ligands, has led to some interesting observations. Both the NMR studies and the molecular structure of complex **1a** show that there is an unusual intramolecular interligand interaction between the bipy ligands and the phenyl-containing hydrazones. Unfortunately these compounds do not emit and it was therefore not possible to investigate whether this interaction influences the photophysical properties of these compounds. The fact that the complexes containing the dihydrazone ligands do not emit and that the electrochemical properties are rather ill defined is somewhat disappointing. However, it is felt that these problems can be overcome by changing the substituents in the dihydrazone ligands as is already shown for compounds **If**–**Ih**. Also, with the analogous osmium compounds the problems with the observed ligand oxidation would be avoided because of the lower oxidation potentials observed for this metal. Finally with ligand **Ie** two reactive amino groups can be introduced into the ruthenium complex which gives the possibility of linking such complexes to other components such as polymers, biological molecules and other metal complexes; in this manner multinuclear structures can be constructed in a controlled manner.

Experimental

Instrumental Procedures.—The purity of the complexes was established using cation-exchange HPLC (Waters 990 photodiode array detector with a NEC PAC III computer). A μ Partisil SCX radial PAK cation cartridge was used, the detection wavelength was 280 nm, and the mobile phase acetonitrile–water (80:20 v/v) containing 0.08 mol dm^{-3} $LiClO_4$ at the flow rate of 2.5 cm^3 min^{-1}. Infrared spectra were recorded on a Perkin Elmer 983-G spectrometer from pressed KBr disks, ^{1}H NMR spectra on a Bruker AC 400 MHz spectrometer calibrated using the residual proton resonance of the solvent, UV/VIS spectra using a Shimadzu UV-240 spectrometer and emission spectra, up to 900 nm, on a Perkin Elmer LS50 luminescence spectrometer in acetonitrile at room temperature and in ethanol at 77 K. Elemental analyses were carried out in the Microanalytical Laboratory, Chemistry Department, University College, Dublin.

Crystal Structure.—The crystal used for analysis was formed by slow recrystallisation of a dilute solution of complex **1a** from acetone–toluene. It diffracted strongly and to a high Bragg angle. Experimental data are listed in Table 6. The asymmetric unit consists of half of the cation, one anion (with 9:1 disorder about one of the F–P–F directions) and one toluene molecule of solvation with a site occupancy of 0.5. The structure was solved by direct methods, SHELX 86,[24] and refined by full-matrix least squares using SHELX 76.[25] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The non-hydrogen atoms of the cation and the atoms of the major orientation of the anion were refined anisotropically. The thermal parameters were terms U_{ij} of $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]$. The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from refs. 26–28. All calculations were performed on a VAX 8700 computer. The ORTEP program[29] was used to obtain the drawings.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Table 6 Crystal data for compound **1a**

Formula	$C_{36}H_{34}F_{12}N_8P_2Ru{\cdot}C_6H_5CH_3$
M	1061.858
Crystal symmetry	Monoclinic
Crystal size (mm)	0.3 × 0.35 × 0.28
Space group	$C2/c$
a/Å	25.895(3)
b/Å	10.505(1)
c/Å	17.431(2)
β/°	106.03(2)
U/Å^3	4557
Z	4
D_c/g cm^{-3}	1.55
μ/cm^{-1}	4.31
F(000)	1952
Mo-Kα Radiation (λ/Å)	0.7093
Diffractometer	Enraf-Nonius CAD4F with graphite monchromator
Orienting reflections, range/°	25, 13 < θ < 20
Temperature (°C)	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 72
No. unique data	6328
Total with $I > 3\sigma(I)$, N_o	3944
No. of parameters fitted, N_p	307
R,[a] R'[b]	0.0463, 0.0527
Quality-of-fit indicator[c]	1.9
Largest shift/e.s.d. in final cycle	<0.001
Largest positive and negative electron-density peak/e Å^{-3}	0.25, −0.14

[a] $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$; $w = 1.59/\{[\sigma(F_o)]^2 - 0.0014F_o^2\}$. [c] $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$.

Materials.—The complex $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ was prepared as previously described.[30] Biacetyl, substituted hydrazines and all other reactants were reagent grade and used as received from the suppliers. All hydrazone ligands were prepared using standard synthetic methods.[10–14]

Synthesis of Ruthenium Complexes.—[*Biacetyl di(phenylhydrazone)*]*bis*(2,2′-*bipyridine*)*ruthenium bis*(*hexafluorophosphate*) **1a**. To a solution of $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (100 mg, 0.19 mmol) in water (40 cm^3) was added biacetyl di(phenylhydrazone) **Ia** (61.4 mg, 0.23 mmol) in ethanol (40 cm^3). After heating under reflux for 24 h the solvent was removed at 90 °C under vacuum. The residue was redissolved in water (10 cm^3) and, following an ether extraction to remove excess of ligand, was added dropwise to a solution of NH_4PF_6 (100 mg) in water (20 cm^3). The precipitate was collected and dried under vacuum. The complex was recrystallised from toluene–acetone to obtain crystals suitable for X-ray crystallography (125 mg, 80%). IR (KBr) 3336 cm^{-1}. ^{1}H NMR [400 MHz, $(CD_3)_2SO$)]: δ 2.8 (s, 6 H), 5.9 (m, 4 H, *ortho*), 6.5 (s, 6 H, *meta* and *para*), 7.2 (d, 2 H^6), 7.3 (t, 2H^5), 7.8 (t, 2 H^4), 7.9 (t, 2 H$^{5'}$), 8.1 (d, 2 H^3), 8.2 (t, 2 H$^{4'}$), 8.25 (d, 2 H$^{3'}$), 8.4 (d, 2 H$^{6'}$) and 9.1 (s, 2H, NH) (Found: C, 42.80; H, 3.50; N, 11.00. $C_{36}H_{34}F_{12}N_8P_2Ru{\cdot}2H_2O$ requires C, 43.00; H, 3.80; N, 11.15%).

{*Biacetyl di*[*methyl*(*phenyl*)*hydrazone*]}*bis*(2,2′-*bipyridine*)-*ruthenium bis*(*hexafluorophosphate*) **1b**. The complex $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (100 mg, 0.19 mmol) in water (40 cm^3) was added to biacetyl di[methyl(phenyl)hydrazone] (280 mg, 0.95 mmol) in ethanol (40 cm^3) and heated under reflux for 48 h. Following the work-up as described for **1a**, complex **1b** was obtained (105 mg, 74%). ^{1}H NMR [400 MHz, $(CD_3)_2SO$, *ca.* 363 K]: δ 2.87 (s, 6 H), 3.04 (s, 6 H), 6.01 (d, 4 H, *ortho*), 6.58 (m, 6 H, *meta* and *para*), 7.03 (d, 2 H^6), 7.17 (t, 2 H^5), 7.82 (t, 2 H^4), 7.86 (t, 2H$^{5'}$), 8.08 (d, 2 H^3), 8.22 (t, 2 H$^{4'}$), 8.27 (d, 2 H$^{3'}$) and 8.86 (d, 2 H$^{6'}$) (Found: C, 46.00; H, 3.90; N, 11.25. $C_{38}H_{38}F_{12}N_8P_2Ru$ requires C, 45.75; H, 3.80; N, 11.25%).

[*Biacetyl di*(o-*tolylhydrazone*)]*bis*(2,2′-*bipyridine*)*ruthenium bis*(*hexafluorophosphate*) **1c**. The complex $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (200 mg, 0.38 mmol) in water (40 cm^3) was added to diacetyl di(*o*-tolylhydrazone) **Ic** (136 mg, 0.46 mmol) in ethanol (40 cm^3) and heated under reflux for 120 h. Following the work-up described for **1a**, complex **1c** was obtained (245 mg, 93%). IR (KBr) 3320 cm^{-1}. ^{1}H NMR [400 MHz, $(CD_3)_2SO$, *ca.* 373 K]: δ 2.00 (s, 6 H), 2.48 (s, 6 H), 5.51 (d, 2 H$^{6''}$), 6.26 (t, 2 H$^{5''}$), 6.58 (t, 2 H$^{4''}$), 6.64 (d, 2 H$^{3''}$), 7.14 (t, 2 H^6), 7.24 (d, 2 H^5), 7.65 (t, H^4), 7.90 (t, 2 H$^{5'}$), 7.95 (d, 2 H^3), 8.23 (t, 2H$^{4'}$), 8.35 (d, 2 H$^{3'}$), 8.69 (d, 2 H$^{6'}$) and 9.05 (s, 2 H, NH) (Found: C, 45.75; H, 3.80; N, 10.75. $C_{38}H_{38}F_{12}N_8P_2Ru$ requires C, 45.75; H, 3.80; N, 11.25%).

[*Biacetyl di*(*methylhydrazone*)]*bis*(2,2′-*bipyridine*)*ruthenium bis*(*hexafluorophosphate*) **1d**. The complex $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (200 mg, 0.38 mmol) in water (40 cm^3) was added to biacetyl di(dimethylhydrazone) **Id** (200 mg, 1.18 mmol) and heated under reflux for 48 h. Following the work-up as for **1a**, complex **1d** was obtained (140 mg, 60%). ^{1}H NMR [400 MHz, $(CD_3)_2SO$]: δ 1.90 (s, 12 H), 2.73 (s, 6 H), 7.33 (t, H^4), 7.67 (d, 2 H^3), 7.78 (t, 2 H$^{4'}$), 8.05 (t, 2 H^5), 8.22 (d, 2 H$^{3'}$), 8.33 (t, 2 H$^{5'}$), 8.73 (d, 2 H^6) and 8.88 (d, 2 H$^{6'}$) (Found: C, 38.45; H, 3.75; N, 12.55. $C_{28}H_{34}F_{12}N_8P_2Ru$ requires C, 38.50; H, 3.90; N, 12.85%).

(*Biacetyl dihydrazone*)*bis*(2,2′-*bipyridine*)*ruthenium bis*(*hexafluorophosphate*) **1e**. The complex $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (200 mg, 0.38 mmol) in water (40 cm^3) was added to diacetyl dihydrazone **Ie** (220 mg, 1.93 mmol) in ethanol (40 cm^3) and heated under reflux for 24 h. Following work-up as for **1a**, complex **1e** was obtained (170 mg, 85%). IR (KBr) 3330 and 3193 cm^{-1}. ^{1}H NMR [400 MHz, $(CD_3)_2SO$]: δ 2.48 (s, 6 H), 6.54 (m, 4 H), 7.36 (t, 2 H^5), 7.44 (d, 2 H^6), 7.78 (t, 2 H$^{4'}$), 8.02 (t, 2 H^4), 8.22 (d, 2 H$^{3'}$), 8.26 (t, 2 H$^{5'}$) and 8.80 (d, 2 H$^{6'}$) (Found: C, 35.25; H, 3.25; N, 13.75. $C_{24}H_{26}F_{12}N_8P_2Ru$ requires C, 35.25; H, 3.20; N, 13.70%).

[*Biacetyl di*(*benzaldehyde azine*)]*bis*(2,2′-*bipyridine*)*ruthenium bis*(*hexafluorophosphate*) **1f**. *Method* (*a*). To complex **1e** (200 mg, 0.38 mmol) in ethanol–acetonitrile–acetic acid (30:20:20 cm^3) was added benzaldehyde (200 mg, 1.90 mmol). The reaction mixture was heated under reflux for 120 h. Following work-up as for **1a**, complex **1f** was isolated (150 mg, 60%). ^{1}H NMR [270 MHz, $(CD_3)_2CO$]: δ 2.8 (s, 6 H), 7.39 (d, 2 H^6), 7.42 (m, 8 H), 7.51 (t, 2 H^5), 7.7 (s, 2 H), 7.85 (t, 2 H^4), 7.94 (t, 2 H$^{5'}$), 8.55 (t, 2 H^3), 8.80 (d, 2 H$^{3'}$), 8.84 (d, 2 H$^{4'}$) and 8.93 (d, 2 H$^{6'}$) (Found: C, 44.20; H, 3.65; N, 10.80. $C_{38}H_{34}F_{12}N_8P_2Ru{\cdot}2H_2O$ requires C, 44.30: H, 3.70; N, 10.90%).

Method (*b*). To a solution of $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (200 mg, 0.38 mmol) in water (40 cm^3), was added diacetyl di(benzaldehyde azine) (200 mg, 0.76 mmol) in ethanol (40 cm^3). The reaction mixture was heated under reflux for 120 h. Following work-up as for **1a** the product **1f** was purified using semi-preparative HPLC [cation-exchange column; mobile phase, acetonitrile–water (80:20 v/v) (0.1 mol dm^{-3} KNO_3)]. It had identical spectral properties to the product obtained using Method (*a*).

(2-*Acetylpyridine phenylhydrazone*)*bis*(2,2′-*bipyridine*)-*ruthenium bis*(*hexafluorophosphate*) **1g**. The complex $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (200 mg, 0.38 mmol) in water (40 cm^3) was added to 2-acetylpyridine phenylhydrazone (160 mg, 0.80 mmol) in ethanol (40 cm^3) and refluxed for 2 h. Following work-up as for **1a**, complex **1g** was isolated (240 mg, 69%). ^{1}H NMR [400 MHz, $(CD_3)_2SO$]: δ 3.00 (s, 3 H), 5.81 (m, 2 H, *ortho*), 6.57 (s, 3 H, *meta* and *para*), 7.33 (2 H, H^6, H$^{5'}$), 7.46 (t, 1 H, H^5), 7.60 (m, 4 H, 2 H^5, 2 H^6), 7.77 (m, 2 H, H^5, H^6), 7.85 (t, 1 H, H$^{4'}$), 8.09 (m, 3 H, 2H^4, H$^{3'}$), 8.17 (m, 3 H, 2 H^4, H^3), 8.47 (1 H, d, H^6), 8.54 (d, 1 H, H^3), 8.76 (q, 2 H, 2 H^3) and 9.0 (s, 1 H, NH) (Found: C, 42.70; H, 3.20; N, 10.50. $C_{33}H_{29}F_{12}N_7P_2Ru$ requires C, 43.35; H, 3.15; N, 10.70%).

(2-*Acetylpyridine hydrazone*)*bis*(2,2′-*bipyridine*)*ruthenium bis*(*hexafluorophosphate*) **1h**. The complex $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (200 mg, 0.38 mmol) in water (40 cm^3) was added to 2-acetylpyridine hydrazone (100 mg, 0.78 mmol) in ethanol (40 cm^3) and heated under reflux for 2 h. Following work-up as for **1a**,

complex **1h** was isolated (140 mg, 44%). IR (KBr) 3417 and 3310 cm $^{-1}$. ^{1}H NMR [400 MHz, $(CD_3)_2SO$]: δ 3.00 (s, 3 H), 7.21 (s, 2 H, NH_2), 7.28 (t, 1 H, $H^{5'}$), 7.41 (t, 1 H, H^5), 7.49 (m, 3 H, H^5, H^6, $H^{6'}$), 7.59 (m, 3 H, H^5, 2 H^6), 7.71 (t, 1 H, H^5), 7.99 (t, 1 H, $H^{4'}$), 8.04 (t, 1 H, H^4), 8.10 (m, 2 H, H^4, $H^{3'}$), 8.20 (m, 2 H, 2 H^4), 8.34 (d, 1 H, H^6) and 8.78 (m, 4 H, 4 H^3) (Found: C, 38.20; H, 2.85; N, 11.70. $C_{27}H_{25}F_{12}N_7P_2Ru$ requires C, 38.65; H, 3.00; N, 11.70%).

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