Synthesis, Spectroscopy, and Electrochemistry of Homo- and Hetero-leptic Ruthenium(II) Complexes of New Pyrazole-containing Bidentate Ligands

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Heteroleptic $[Ru(bipy)_2(L–L')]^{2+}$ and homoleptic $[Ru(L–L')_3]^{2+}$ complexes, where bipy = 2,2'-bipyridine and L–L' is one of nine new pyrazole-containing bidentate ligands, have been prepared. Full assignments have been made for the ^1H and ^{13}C n.m.r. spectra of the complexes in CD_3CN and the origins of the co-ordination-induced shifts are discussed. The absorption spectra and redox properties of the complexes are also discussed.

Over the last decade there has been intense interest in the redox and photophysical properties of the $[Ru(bipy)_3]^{2+}$ cation,† with emphasis on the electron-transfer processes involved in the photochemical decomposition of water.[1–4] Much of the recent work in this area has centred on attempts to tune the ground- and excited-state properties of related complexes by replacing one or all of the bipy ligands with other N,N'-chelating ligands.[1] In particular numerous complexes have been reported which contain as ligands variously substituted 2,2'-bipyridines,[1,5–8] benzo-annelated 2,2'-bipyridines,[1,9,10] 3,3'-annelated 2,2'-bipyridines,[11] bidiazines,[1,12,13] and in a recent report an encapsulating cage ligand.[14] Further fine tuning has recently been attempted by preparing tris-heteroleptic ruthenium(II) complexes containing such ligands.[15,16] Most of these studies have utilised six-membered aromatic nitrogen heterocycles (azines). However there have been an increasing number of recent reports of studies involving ligands which contain five-membered aromatic heterocycles (azoles), such as imidazoles,[17–19] thiazoles,[19,20] pyrazoles,[21–23] triazoles,[23–25] and their benzo derivatives.[1] Such ligands can greatly modify the properties of the resulting ruthenium complexes, principally due to the very different π-acceptor properties of the π-excessive azoles relative to the π-deficient azines.

In spite of this activity a recent survey[26] of currently available N,N'-chelating biheteroaromatic ligands emphasised the relatively restricted number of such ligands which have hitherto been studied by co-ordination chemists. For example although many pyrazole-derived ligands are known,[27] very few biheteroaromatic pyrazoles have been used as ligands. Some ruthenium(II) complexes of pyrazolylpyridines have been reported.[21–23] In an endeavour to extend the range of available chelating heteroaromatic pyrazole ligands, we recently reported[28] the preparation of nine new bidentate ligands each of which consists of a pyrazole linked through nitrogen to another heterocycle which possesses an adjacent nitrogen. This second heterocycle was chosen to be either a diazine, quinoline, or thiazole in line with the current interest in ligands containing these groups.[1] We herein report the first studies of the co-ordination chemistry of these new ligands by describing the preparations and spectroscopic and redox properties of their homo- and hetero-leptic ruthenium(II) complexes. In particular we report detailed n.m.r. studies which probe the effect of small changes within the ligand structure on the overall properties of the complexes.

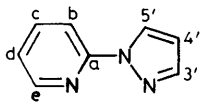
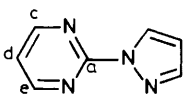
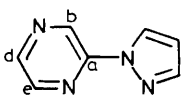
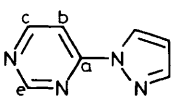
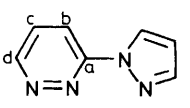
Results and Discussion

Preparation of Complexes.—The previously studied[23] ligand (**1**) and the new[28] pyrazole-containing ligands (**2**)—(**9**) were each treated with $[Ru(bipy)_2Cl_2]$ to give the heteroleptic $[Ru(bipy)_2(L–L')]^{2+}$ complexes (**11**)—(**19**) which were isolated as the hexafluorophosphate salts. The properties of these complexes are discussed below. A similar reaction with (**10**) gave a product which was clearly not the expected complex (**20**) since the proton n.m.r. spectrum showed signals for only 19 aromatic protons rather than the expected 23 protons. Furthermore the presence of a signal at δ 9.89 was indicative of a bipy H^6 deshielded by a co-ordinated chloride {*cf.* $[Ru(bipy)_2Cl_2]$: H^6, δ 9.89[29]}. The product was identified by n.m.r. and elemental analysis as $[Ru(bipy)_2(Hpz)Cl]PF_6$; the pyrazole (Hpz) results from decomposition of the ligand (**10**) presumably by solvolytic ring opening of the benzoxazole.

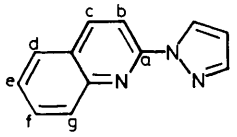
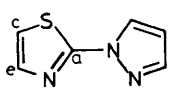
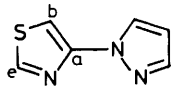
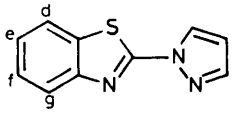
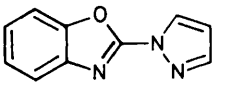
Reaction of $[Ru(dmso)_4Cl_2]$ (dmso = dimethyl sulphoxide) with the ligands (**1**)—(**5**) gave the homoleptic $[Ru(L–L')_3]^{2+}$ complexes (**21**)—(**25**) in reasonable yields. The corresponding reactions with ligands (**6**)—(**8**) produced complex mixtures of products which, although containing the desired products (**26**)—(**28**), were not readily purified and therefore not further investigated. The benzothiazole (**9**) did however give the desired complex (**29**) as the major product. Since the ligands employed are unsymmetrical, the homoleptic $[Ru(L–L')_3]^{2+}$ complexes can exist as meridional (*mer*) and facial (*fac*) isomers. N.m.r. spectra showed that the complexes (**21**)—(**25**) were each formed in the statistically expected 3:1 ratio of *mer*:*fac* isomers. However a solution of (**22**) underwent photoisomerisation to give quantitatively the more stable *mer* isomer when exposed to sunlight for several days. Furthermore the complex (**29**) was formed almost exclusively as the *mer* isomer presumably because the *fac* isomer is destabilised by steric interactions between the bulky benzothiazole rings.

Proton N.M.R. Spectra.—The proton chemical shifts for ruthenium(II) complexes of this type are highly solvent dependent. For example chemical shifts have been reported for $[Ru(bipy)_3]^{2+}$ in deuteriated acetonitrile,[11,20,21] dimethyl sulphoxide,[23,30,31] and acetone[32,33] solutions and differences of up to 0.5 p.p.m. exist between chemical shifts measured in different solvents. Accordingly all the proton and carbon-13

† Ligand abbreviations: bipy = 2,2'-bipyridine, Hpz = pyrazole, pzpy = 2-(1'-pyrazolyl)pyridine, pzpm = 2-(1'-pyrazolyl)pyrimidine, pzprz = 2-(1'-pyrazolyl)pyrazine, pzipm = 4-(1'-pyrazolyl)pyrimidine, pzpdz = 3-(1'-pyrazolyl)pyridazine, pzqu = 2-(1'-pyrazolyl)quinoline, pzth = 2-(1'-pyrazolyl)thiazole, pzith = 4-(1'-pyrazolyl)thiazole, pzbth = 2-(1'-pyrazolyl)benzothiazole, pzbox = 2-(1'-pyrazolyl)-benzoxazole.

L–L′	(1)	(2)	(3)	(4)	(5)
$[Ru(bipy)_2(L–L')]^{2+}$	(11)	(12)	(13)	(14)	(15)
$[Ru(L–L')_3]^{2+}$	(21)	(22)	(23)	(24)	(25)

L–L′	(6)	(7)	(8)	(9)	(10)
$[Ru(bipy)_2(L–L')]^{2+}$	(16)	(17)	(18)	(19)	(20)
$[Ru(L–L')_3]^{2+}$	(26)	(27)	(28)	(29)	

n.m.r. spectra reported here were recorded in the same solvent, *viz.* CD_3CN. The spectra of the free ligands (**1**)—(**9**) were assigned by comparison of chemical shifts and coupling constants with the previously assigned[28] spectra recorded in $CDCl_3$. Table 1 lists the ^1H n.m.r. chemical shifts for the ligands (**1**)—(**9**) and complexes (**11**)—(**29**) with co-ordination-induced shifts (c.i.s. = $\delta_{complex} - \delta_{ligand}$), in parentheses.

Because of the absence of symmetry in the $[Ru(bipy)_2(L–L')]^{2+}$ complexes up to 25 non-equivalent aromatic proton resonances exist for the 16 bipy protons plus the protons of the pyrazole-containing ligand. In most cases sufficient resolution exists at 400 MHz to locate each proton unambiguously. It has recently been shown[34] that such spectra can be greatly simplifed by utilising perdeuteriobipyridine as the ancillary ligand, thereby removing the 16 bipy proton signals from the ^1H n.m.r. spectrum. In the present study this was not necessary and the additional information available from the bipy proton chemical shifts was retained.

For the complexes (**11**)—(**19**) assignments were made by comparison with the spectra of the free ligands and of related complexes from the literature.[21–23,25,30–34] In some cases one-dimensional decoupling experiments or two-dimensional correlation spectroscopy (COSY) was used to resolve ambiguities as has previously been reported for related complexes.[20,25,35–38] In the case of the complex (**16**) neither the proton nor the carbon-13 n.m.r. spectrum could be unambiguously assigned by these techniques due to substantial overlap of signals. However both spectra were completely assigned with the aid of a two-dimensional proton–carbon heteronuclear correlation spectrum. For example correlation of the four well resolved bipy H^3 protons at δ 8.37—8.56 with four signals in the carbon dimension at 124.9—125.3 p.p.m. allowed assignment of the nearby (125.6 p.p.m.) carbon signal to C_g in the ligand (**6**) and this in turn could be back correlated to the doublet at δ 7.223 in the proton dimension. Conversely, although only one of the four bipy H^6 protons was not overlapping other proton signals, the remaining three were straightforwardly located by correlation to the characteristic signals at *ca.* 153 p.p.m. in the carbon dimension.

The spectra for the homoleptic $[Ru(L–L')_3]^{2+}$ complexes (**21**)—(**25**) and (**29**) were generally more well dispersed and more readily assigned because of the characteristic proton–proton coupling constants of the pyrazole and azine ring protons. Where necessary ambiguities were resolved by methods similar to those described above. As mentioned above complexes (**21**)—(**25**) exist as a 3:1 mixture of *mer*:*fac* isomers. However no attempt was made to assign signals to specific ligands within the unsymmetrical *mer* and symmetrical *fac* isomers, as has recently been achieved for related complexes.[20]

The only compound which has been previously described is the complex (**11**). Although the previously reported[23] proton n.m.r. spectrum for (**11**) was recorded (at 200 MHz) as a dmso solution, the reported assignments and c.i.s. values are greatly different from our values in Table 1. Since these differences could not be solely due to solvent effects, we rerecorded the spectra for the free ligand (**1**) and its complex (**11**) in $(CD_3)_2SO$. At 400 MHz all seven protons of (**1**) are well resolved. The well established[39] observation that $^3J(H^{4'}H^{5'})$, is substantially greater than $^3J(H^{3'}H^{4'})$ led to a reversal of the previous[23] assignments for $H^{3'}$ and $H^{5'}$ in the pyrazole ring, in agreement with a more recent report[40] of the spectrum of (**1**) in $(CD_3)_2SO$. Similarly the signal at δ 9.36 in the spectrum of complex (**11**) should be assigned to $H^{5'}$ rather than $H^{3'}$ which in fact resonates at δ 7.56. Thus only one proton appears at δ 8.46 rather than the two previously reported.[23] Furthermore the proton at δ 7.92 does not belong to the ligand (**1**), but rather to one of the bipy ligands (specifically the H^6 proton of the pyridine ring which lies over the plane of the pyrazole ring of (**1**) since this ring is well known[21] to be less strongly shielding than the pyridine rings which shift the other three bipy H^6 protons to higher field). In fact H^6 of the ligand (**1**) resonates at δ 7.59 which leads to a more realistic c.i.s. value of −0.87 p.p.m.

Inspection of the chemical shift and c.i.s. values in Table 1 allows a number of observations to be made. The c.i.s. values are, in general, positive except for protons on carbon atoms adjacent to the co-ordinating nitrogens. These protons show significant negative (upfield) c.i.s. values, which are always greater for the heteroleptic complexes (**11**)—(**19**) than for the homoleptic complexes (**21**)—(**29**). In contrast other protons generally have the same (±0.1 p.p.m.) c.i.s. values in their respective heteroleptic and homoleptic complexes. In the heteroleptic complexes (**11**)—(**19**) the 16 bipy protons resonate at characteristic chemical shifts for the different positions in the pyridine ring (standard deviations in parentheses): H^3, δ 8.49 (0.03); H^4, 8.08 (0.03); H^5, 7.43 (0.03); H^6, 7.83 (0.14). Thus of the bipy protons H^6 exhibits by far the greatest spread in chemical shift, ranging from 7.5—8.1 p.p.m.

In a recent study[20] of the ^1H n.m.r. spectra of a series of related homoleptic complexes the authors identified and

Table 1. Proton n.m.r. chemical shifts and co-ordination-induced shifts

	$H^{3'}$	$H^{4'}$	$H^{5'}$	H_b	H_c	H_d	H_e	H_f	H_g	H^3	H^4	H^5	H^6
(1)	7.741	6.506	8.570	7.959	7.893	7.265	8.417						
										8.483	8.048	7.372	7.763
(11)	7.345	6.788	8.768	8.079	8.105	7.290	7.594			8.509	8.070	7.412	7.785
(11) − (1)	(−0.40)	(+0.28)	(+0.20)	(+0.12)	(+0.31)	(+0.03)	(−0.82)			8.509	8.070	7.450	7.863
										8.509	8.087	7.474	7.912
(21)	7.424	6.785	8.738	8.026	8.095	7.281	7.712						
	7.447	6.787	8.746	8.046	8.102	7.305	7.728						
	7.453	6.812	8.758	8.046	8.118	7.323	7.752						
	7.481	6.818	8.766	8.046	8.126	7.342	7.768						
(21) − (1)	(−0.29)	(+0.30)	(+0.18)	(+0.08)	(+0.22)	(+0.05)	(−0.68)						
(2)	7.789	6.525	8.603		8.765	7.318	8.765						
										8.482	8.048	7.375	7.730
(12)	7.415	6.802	8.883		8.851	7.348	7.946			8.494	8.068	7.404	7.767
(12) − (2)	(−0.37)	(+0.28)	(+0.23)		(+0.09)	(+0.03)	(−0.82)			8.513	8.116	7.479	7.928
										8.513	8.116	7.509	8.077
(22)	7.532	6.825	8.818		8.868	7.384	8.099						
	7.577	6.833	8.826		8.875	7.405	8.135						
	7.685	6.846	8.838		8.880	7.407	8.280						
	7.736	6.854	8.844		8.890	7.431	8.324						
(22) − (2)	(−0.16)	(+0.31)	(+0.23)		(+0.11)	(+0.09)	−(0.56)						
(3)	7.818	6.569	8.536	9.254		8.504	8.404						
										8.492	8.065	7.392	7.724
(13)	7.400	6.843	8.848	9.280		8.381	7.644			8.503	8.084	7.417	7.746
(13) − (3)	(−0.42)	(+0.27)	(+0.31)	(+0.03)		(−0.12)	(−0.76)			8.511	8.111	7.449	7.822
										8.511	8.114	7.491	7.928
(23)	7.484	6.876	8.850	9.297		8.433	7.718						
	7.521	6.876	8.865	9.297		8.463	7.745						
	7.617	6.899	8.865	9.307		8.473	7.864						
	7.650	6.899	8.875	9.307		8.498	7.880						
(23) − (3)	(−0.25)	(+0.32)	(+0.33)	(+0.05)		(−0.04)	(−0.60)						
(4)	7.822	6.564	8.833	7.897	8.767		8.975						
										8.460	8.038	7.357	7.459
(14)	7.427	6.843	8.820	8.000	8.896		8.283			8.477	8.049	7.385	7.679
(14) − (4)	(−0.40)	(+0.28)	(+0.21)	(+0.10)	(+0.13)		(−0.69)			8.491	8.095	7.449	7.773
										8.493	8.098	7.473	7.820
(24)	7.485	6.860	8.808	7.993	8.911		8.309						
	7.581	6.872	8.817	7.993	8.920		8.417						
	7.647	6.880	8.822	7.993	8.920		8.514						
	7.744	6.880	8.829	7.993	8.931		8.616						
(24) − (4)	(−0.21)	(+0.31)	(+0.21)	(+0.10)	(+0.25)		(−0.51)						
(5)	7.840	6.599	8.764	8.192	7.728	9.089							
										8.425	8.025	7.349	7.685
(15)	7.438	6.847	8.763	8.257	7.856	8.775				8.454	8.074	7.409	7.843
(15) − (5)	(−0.40)	(+0.25)	(0)	(+0.07)	(+0.13)	(−0.31)				8.501	8.084	7.433	7.843
										8.510	8.096	7.467	7.900
(25)	7.479	6.811	8.669	8.194	7.876	8.793							
	7.526	6.828	8.727	8.233	7.898	8.797							
	7.685	6.864	8.737	8.248	7.905	8.797							
	7.755	6.882	8.780	8.271	7.909	8.856							
(25) − (5)	(−0.23)	(+0.25)	(−0.04)	(+0.04)	(+0.17)	(−0.28)							
(6)	7.803	6.571	8.766	8.174	8.381	7.924	7.549	7.759	7.958				
										8.372	7.966	7.339	7.583
(16)	7.249	6.870	8.943	8.190	8.655	8.027	7.578	7.339	7.223	8.451	8.070	7.358	7.641
(16) − (6)	(−0.55)	(+0.30)	(+0.18)	(+0.02)	(+0.27)	(+0.10)	(+0.03)	(−0.42)	(−0.74)	8.510	8.089	7.393	8.006
										8.560	8.089	7.494	8.117
(7)	7.746	6.538	8.373		7.270		7.559						
										8.472	8.037	7.370	7.771
(17)	7.408	6.777	8.652		7.617		6.908			8.473	8.048	7.385	7.799
(17) − (7)	(−0.34)	(+0.24)	(+0.28)		(+0.35)		(−0.65)			8.488	8.100	7.496	7.933
										8.497	8.100	7.500	7.933
(8)	7.692	6.467	8.315	7.498			8.888						
										8.473	8.034	7.368	7.779
(18)	7.242	6.705	8.635	7.999			8.283			8.485	8.053	7.368	7.818
(18) − (8)	(−0.45)	(+0.24)	(+0.32)	(+0.50)			(−0.61)			8.505	8.101	7.488	7.932
										8.507	8.101	7.492	7.980
(9)	7.820	6.613	8.505			7.878	7.405	7.515	7.949				
										8.457	8.050	7.381	7.718
(19)	7.447	6.871	8.776			8.118	7.499	7.260	6.165	8.493	8.070	7.416	7.860
(19) − (9)	(−0.37)	(+0.26)	(+0.27)			(+0.24)	(+0.09)	(−0.26)	(−1.78)	8.523	8.107	7.481	7.961
										8.531	8.150	7.497	8.043

Table 1. (*continued*)

	$H^{3'}$	$H^{4'}$	$H^{5'}$	H_b	H_c	H_d	H_e	H_f	H_g	H^3	H^4	H^5	H^6
(29)	7.700	6.873	8.806			8.073	7.448	7.170	6.195				
	7.750	6.978	8.836			8.134	7.516	7.385	6.314				
	7.877	6.990	8.886			8.146	7.584	7.483	6.508				
(29) − (9)	(−0.04)	(+0.34)	(+0.34)			(+0.24)	(+0.11)	(−0.17)	(−1.61)				

attempted to quantify four contributing factors to the observed c.i.s. values. Positive contributions were attributed to ligand-to-metal σ donation and to increased van der Waals interactions resulting from changes in ligand conformation upon co-ordination. Negative contributions were attributed to metal-to-ligand π-back donation and to through-space ring-current anisotropy effects. For complexes (**11**)—(**29**) the principal contribution to the downfield shifts undoubtedly arises from σ donation. Thus the c.i.s. values for the diazine ring protons (H_b—H_e) for complexes of ligands (**2**)—(**6**) are all less positive than those for complexes of (**1**). This is in accord with the well established fact that diazines are poorer σ donors and better π acceptors than pyridine.[13] Chelation-imposed van der Waals interactions are restricted to protons (H_b and $H^{5'}$) *ortho* to the inter-ring linkage. The resulting contributions to the c.i.s. values are more difficult to assess since these will depend on the conformation of the free ligand and the nature of the interacting groups (CH, N, or S) in the complexes. Such contributions could in fact be either positive or negative in sign but, as recently suggested,[20] are probably less than had earlier been believed.

The large negative c.i.s. values for protons adjacent to co-ordinating nitrogens result from through-space ring-current anisotropy effects. In an octahedral tris(biheteroaromatic) co-ordination environment these protons lie directly over the shielding plane of another aromatic ring. In the heteroleptic complexes (**11**)—(**19**) these protons all lie over a pyridine ring but the c.i.s. values for a proton in a five-membered ring (*e.g.* $H^{3'}$) are all less than those in a six-membered ring [*e.g.* H_e in (**11**)—(**15**)]. This is due to geometrical factors since the protons of the six-membered ring more closely approach the plane of the auxiliary bipy pyridine ring. In a similar way the largest upfield shift is observed for H_g in (**19**) since this proton very strongly interacts with one of the bipy pyridine rings. For the complex (**16**), $H^{3'}$ exhibits a larger than usual upfield shift whilst H_g is less strongly shielded than H_g in (**19**). This may indicate an unusual mode of co-ordination by ligand (**6**) wherein steric interactions are relieved by lengthening of the Ru–N(quinoline) bond and by twisting about the inter-ring bond, as was observed[41] in the crystal structure of a substituted derivative of (**6**).

The through-space ring-current anisotropy effect is also responsible for the observation that, of the bipy protons in complexes (**11**)—(**19**), H^6 shows the greatest variation in chemical shift. For each of these complexes all four bipy H^6 protons are non-equivalent and lie over the shielding plane of another aromatic ring; two lie above adjacent bipy pyridine rings and each of the remaining two lie above one of the rings of the unsymmetrical ligands (**1**)—(**9**). Since ring-current-induced fields depend on the aromaticity and π polarisability of the heterocycle these effects will differ significantly for the different types of heterocycle (pyridine, diazine, pyrazole, or thiazole). For example a pyridine ring is well known[21] to induce greater upfield shifts than a pyrazole ring. This latter fact is also responsible for the observation that the upfield shifts observed for $H^{3'}$ are greater for the heteroleptic complexes (**11**)—(**19**) than the mean values for the homoleptic complexes (**21**)—(**29**) since in (**11**)—(**19**) $H^{3'}$ is shielded by a pyridine ring while in (**21**)—(**29**) two of the four $H^{3'}$ protons are shielded by pyrazole rings.

Assessment of the contribution of metal-to-ligand back bonding to the c.i.s. values is rather difficult and will depend on the π*-orbital coefficients at each site.[20] Furthermore since the ligands (**1**)—(**6**) contain a π-excessive (pyrazole) heterocycle directly bound to a π-deficient (azine) heterocycle there is likely[42] to be conjugation between the rings in the free (uncomplexed) ligand with donation of π-electron density from the pyrazole to the azine. This conjugation is likely to be disrupted by co-ordination to the ruthenium which can act as an alternative acceptor of π-electron density from the pyrazole and π donor to the azine.

Carbon-13 N.M.R. Spectra.—The ^{13}C n.m.r. chemical shifts recorded in CD_3CN for the ligands (**1**)—(**9**) and complexes (**11**)—(**29**) are given in Table 2. Co-ordination-induced shifts are given in parentheses. Assignments for the free ligands in $CDCl_3$ have been previously reported.[28,40] Due to the greater dispersion in ^{13}C n.m.r. spectra relative to ^1H n.m.r., assignments for the heteroleptic complexes (**11**)—(**19**) were generally straightforward. The 20 signals for the bipy carbons appear at very characteristic positions (with very small standard deviations) for each carbon in the pyridine ring. The various signals for the pyrazole-containing ligand in both the homo- and hetero-leptic complexes were generally well resolved and assignments were made by comparison with the spectra of the free ligands and related literature spectra.[20–23,31,43,44] Where necessary any remaining ambiguities were resolved by means of two-dimensional heteronuclear correlation to the previously assigned ^1H n.m.r. spectra, as described above. The only previously reported spectrum is that of complex (**11**) recorded in $(CD_3)_2SO$. Our assignments agree with those of this previous report[23] except that C_d resonates at 124.8 p.p.m. rather than the tentatively reported value of 127.4 p.p.m.

The main contributor to the ^{13}C n.m.r. c.i.s. values appears to be ligand-to-metal σ donation and as a result the c.i.s. values are generally positive. In contrast to the ^1H c.i.s. values, this is also the case for carbons adjacent to the co-ordinating nitrogens since through-space ring-current anisotropy effects are less important in ^{13}C n.m.r. spectra. The only strongly negative c.i.s. values are due to C_g in complexes of the benzo ligands (**6**) and (**9**), and this is attributed to upfield steric-compression effects.[45] It is noteworthy that the other carbon atoms in the benzo ring of these complexes also show significant (downfield) c.i.s. values, a fact which suggests *d*–π metal–ligand orbital interaction with these rings. As was observed in the ^1H n.m.r. spectra of complexes of the ligands (**2**)—(**5**), the c.i.s. values for the diazine ring carbons are less than those of the corresponding carbons in complexes of (**1**) which again reflects the weaker σ-donating ability of the diazine rings relative to a pyridine ring. The pyrazole carbons exhibit the largest c.i.s. values since this π-excessive heterocycle is both a σ and π donor. Of these carbons $C^{4'}$ and $C^{5'}$ exhibit similar c.i.s. values in the heteroleptic and homoleptic complexes but $C^{3'}$ exhibits larger values in the homoleptic complexes. This is a reflection of the weaker σ-donating π-acceptor ability of pyrazoles relative to pyridine[21] and the fact that $C^{3'}$ is more sensitive to σ-donation effects than is $C^{4'}$ or $C^{5'}$.

Absorption Spectra and Redox Properties.—Table 3 lists the electronic absorption spectra for the complexes (**11**)—(**29**). In

Table 2. Carbon-13 n.m.r. chemical shifts and co-ordination-induced shifts

	$C^{3'}$	$C^{4'}$	$C^{5'}$	C_a	C_b	C_c	C_d	C_e	C_f	C_g	C^2	C^3	C^4	C^5	C^6
(1)	142.79	108.61	127.70	152.85	112.95	139.95	122.54	149.05							
											157.77	124.94	138.55	127.90	152.55
(11)	145.56	112.44	132.72	151.40	113.68	140.80	124.76	151.47			157.98	125.01	138.67	128.24	152.85
(11) − (1)	(+2.8)	(+3.8)	(+5.0)	(−1.0)	(+0.7)	(+0.8)	(+2.2)	(+2.4)			158.28	125.07	138.67	128.33	152.90
											158.28	125.07	138.70	128.44	153.07
(21)	146.11	112.01	132.53	151.79	113.37	140.85	124.41	151.99							
	146.29	112.12	132.65	151.83	113.40	140.90	124.60	152.12							
	146.36	112.27	132.75	151.96	113.61	140.99	124.81	152.30							
	146.54	112.37	132.85	151.99	113.64	141.04	125.00	152.44							
(21) − (1)	(+3.5)	(+3.6)	(+5.0)	(−0.5)	(+0.6)	(+1.0)	(+2.2)	(+3.2)							
(2)	143.98	109.20	130.17	156.80		159.88	120.01	159.88							
											157.77	124.86	138.79	128.00	152.95
(12)	147.48	112.92	133.57	156.92		159.85	121.70	161.56			157.95	125.05	138.92	128.33	153.13
(12) − (2)	(+3.5)	(+3.7)	(+3.4)	(+0.1)		(0)	(+1.7)	(+1.7)			158.35	125.15	138.99	128.39	153.23
											158.42	125.20	139.06	128.72	153.33
(22)	148.72	112.42	133.60	156.97		160.15	120.95	162.34							
	148.74	112.63	133.69	157.02		160.23	121.17	162.53							
	149.00	112.63	133.84	157.14		160.33	121.38	162.88							
	149.03	112.83	133.92	157.19		160.33	121.60	163.12							
(22) − (2)	(+4.9)	(+3.4)	(+3.6)	(+0.3)		(+0.4)	(+1.3)	(+2.8)							
(3)	143.83	109.45	128.32	148.34	136.11		143.04	143.04							
											157.76	125.05	139.16	128.25	152.94
(13)	146.52	113.24	133.31	148.43	135.74		144.82	145.62			157.91	125.24	139.29	128.49	153.01
(13) − (3)	(+2.7)	(+3.8)	(+5.0)	(+0.1)	(−0.4)		(+1.8)	(+2.6)			158.04	125.34	139.29	128.66	153.22
											158.38	125.40	139.46	128.85	153.22
(23)	147.69	112.81	133.39	147.94	135.67		144.17	145.79							
	147.69	113.01	133.51	148.05	135.70		144.53	145.94							
	147.94	113.07	133.66	148.19	135.81		144.57	146.25							
	147.94	113.25	133.75	148.27	135.86		144.90	146.37							
(23) − (3)	(+4.0)	(+3.6)	(+5.3)	(−0.2)	(−0.4)		(+1.5)	(+3.0)							
(4)	144.75	109.64	128.44	158.74	110.04	159.25		160.03							
											157.79	124.87	138.83	128.06	152.80
(14)	147.65	113.86	134.12	156.87	109.38	159.54		160.76			157.91	125.04	138.93	128.26	152.98
(14) − (4)	(+2.9)	(+4.2)	(+5.7)	(−1.9)	(−0.7)	(+0.3)		(+0.7)			158.31	125.23	138.97	128.38	153.21
											158.31	125.23	139.04	128.58	153.45
(24)	148.78	113.41	134.21	*a*	109.24	160.02		161.09							
	148.98	113.55	134.36	*a*	109.36	160.02		161.43							
	149.18	113.60	134.49	*a*	109.36	160.06		161.71							
	149.44	113.73	134.64	*a*	109.52	160.17		162.08							
(24) − (4)	(+4.4)	(+3.9)	(+6.0)		(−0.7)	(+0.8)		(+1.5)							
(5)	143.86	109.63	128.11	155.55	118.20	130.34	151.36								
											157.81	124.38	138.58	127.69	152.64
(15)	146.41	113.10	133.72	154.77	119.38	129.66	152.55				157.85	124.72	138.87	127.94	152.93
(15) − (5)	(+3.6)	(+3.5)	(+5.6)	(−0.8)	(+1.2)	(−0.7)	(+1.2)				157.98	124.82	138.93	128.36	152.93
											158.21	124.99	139.10	128.39	153.02
(25)	146.49	112.62	132.72	*a*	118.53	130.31	151.88								
	146.82	112.62	132.80	*a*	118.73	130.51	151.88								
	147.56	112.70	133.40	*a*	119.03	130.53	152.29								
	147.82	112.79	133.59	*a*	119.35	130.81	152.43								
(25) − (5)	(+3.3)	(+3.1)	(+5.0)		(+0.7)	(+0.2)	(+0.8)								
(6)[b]	143.14	109.19	127.90	151.07	112.92	140.21	128.77	126.67	131.33	128.91					
											157.92	124.87	138.62	128.29	152.45
(16)[c]	146.40	113.11	133.87	151.55	112.02	142.84	130.72	128.76	133.39	125.59	158.00	125.08	138.82	128.34	152.69
(16) − (6)	(+3.3)	(+3.9)	(+6.0)	(+0.5)	(−0.9)	(+2.6)	(+20)	(+2.1)	(+2.1)	(−3.3)	158.35	125.30	138.88	128.52	153.26
											158.72	125.34	139.04	128.83	153.58
(7)	143.53	109.52	128.31	162.41		117.43		141.11							
											157.92	124.80	138.56	127.91	152.96
(17)	146.45	113.03	134.05	159.59		120.94		139.57			157.92	124.80	138.67	128.09	153.29
(17) − (7)	(+2.9)	(+3.5)	(+5.7)	(−2.8)		(+3.5)		(−1.5)			158.11	124.93	138.67	128.39	153.36
											158.11	124.93	138.75	128.53	153.41
(8)	142.40	107.78	129.08	*a*	103.24			154.70							
											158.01	124.77	138.50	127.90	152.65
(18)	144.56	112.15	132.33	147.91	105.13			157.39			158.03	124.87	138.58	128.01	152.83
(18) − (8)	(+2.2)	(+4.4)	(+3.3)		(+3.4)			(+2.7)			158.57	124.90	138.66	128.23	153.31
											158.76	124.98	138.71	128.39	153.51
(9)[d]	144.43	110.48	128.99	*a*			123.02	125.92	127.64	122.88					
											157.84	124.87	138.82	128.14	153.05
(19)[e]	147.62	114.02	134.84	159.60			125.04	128.72	129.57	119.71	158.00	124.98	138.82	128.17	153.34
(19) − (9)	(+3.2)	(+3.5)	(+5.9)				(+2.0)	(+2.8)	(+1.9)	(−3.2)	158.82	125.11	138.92	128.52	153.43
											159.04	125.30	139.18	128.56	154.25

Table 2. (*continued*)

	$C^{3'}$	$C^{4'}$	$C^{5'}$	C_a	C_b	C_c	C_d	C_e	C_f	C_g	C^2	C^3	C^4	C^5	C^6
(29)[f]	149.30	113.77	135.15	159.99			124.97	128.14	129.61	119.49					
	150.10	114.35	135.21	160.27			124.97	128.14	129.82	119.71					
	150.16	114.42	135.21	160.76			125.40	128.46	130.34	119.84					
(29) − (9)	(+5.4)	(+3.7)	(+6.2)				(+2.1)	(+2.3)	(+2.3)	(−3.2)					

[a] Not observed. [b] C^{8a}, 147.21 p.p.m. [c] C^{4a}, 128.60; C^{8a}, 148.96 p.p.m. [d] C^{3a}, C^{7a} not observed. [e] C^{3a}, 149.08; C^{7a}, 131.76 p.p.m. [f] C^{3a}, 149.30, 149.35, 149.40; C^{7a}, 131.35, 131.45, and 131.45 p.p.m.

Table 3. Electronic absorption spectra *

	$[Ru(bipy)_2(L–L')]^{2+}$						$[Ru(L–L')_3]^{2+}$			
(11)	442	408	367	283	243	**(21)**	371	275	250	221
	(1.06)	(1.02)	(0.85)	(6.55)	(2.68)		(1.29)	(4.73)	(2.76)	(2.16)
(12)	430	410	370	285	254, 245	**(22)**	368	260		222
	(1.12)	(1.12)	(0.69)	(5.14)	(2.80, 2.80)		(1.47)	(4.30)		(2.74)
(13)	427			284	247	**(23)**	391	285	252	231
	(1.39)			(5.88)	(2.70)		(1.27)	(3.14)	(3.06)	(2.74)
(14)	428			281	245	**(24)**	390	274		
	(1.22)			(5.36)	(2.38)		(1.21)	(4.94)		
(15)	429			284	245	**(25)**	397	266	251	
	(1.33)			(4.96)	(2.58)		(1.35)	(2.70)	(3.06)	
(16)	433			286	267, 257, 242					
	(1.31)			(6.21)	(3.64, 3.39, 3.60)					
(17)	442	408	376	285	244					
	(1.06)	(0.98)	(0.65)	(6.58)	(2.27)					
(18)	445	402		286	255					
	(0.97)	(0.74)		(5.50)	(2.77)					
(19)	427		382	318, 285	245	**(29)**	387	317, 275	248	
	(1.07)		(0.57)	(1.71, 5.62)	(2.28)		(1.07)	(3.37, 3.70)	(2.55)	

* Absorption maxima in nm; measured in acetonitrile; $\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1} in parentheses.

Table 4. Redox potentials[a]

Complex	$E^{2+/3+}$	$E^{2+/1+}$	$\Delta E_{ox\text{-}red}$
$[Ru(bipy)_3]^{2+}$	+1.26	−1.36	2.62
(11)	+1.26	−1.39	2.65
(12)	+1.30	−1.36[b]	2.66
(13)	+1.35	−1.33	2.68
(14)	+1.35	−1.34[b]	2.69
(15)	+1.29	−1.40[b]	2.69
(16)	+1.28	−1.33[b]	2.61
(17)	+1.28	−1.42	2.70
(18)	+1.24	−1.40	2.64
(19)	+1.30	−1.42[b]	2.72
(21)	+1.29	−1.76[b]	3.05
(22)	+1.46	−1.42[b]	2.88
(25)	+1.41	−1.38[b]	2.79
(29)	+1.48	−1.48[b]	2.96

[a] In volts *vs.* s.c.e. in acetonitrile. [b] Irreversible (approximate value estimated from anodic half-scan).

all cases the strongest absorption occurs near 280 nm and these peaks correspond to ligand-based $\pi \longrightarrow \pi^*$ transitions. The lowest-energy absorptions occur around 435 nm for the heteroleptic $[Ru(bipy)_2(L–L')]^{2+}$ complexes **(11)**—**(19)** and around 380 nm for the homoleptic $[Ru(L–L')_3]^{2+}$ complexes **(21)**—**(29)**; these are assigned as metal-to-ligand charge-transfer (m.l.c.t.) bands. As has been previously noted[21,46,47] the spectra for the heteroleptic complexes resemble the statistically averaged spectra for the corresponding component homoleptic complexes {*i.e.* $\frac{2}{3}[Ru(bipy)_3]^{2+}$, $\lambda_{max.}$ 450 nm; $\frac{1}{3}[Ru(L–L')_3]_2^{+}$}. The oxidation and first reduction potentials are listed in Table 4. In most cases the reduction potentials are only approximate since the ligand-based reductions were often irreversible processes.

The m.l.c.t. transitions occur at much higher energy in the homoleptic complexes **(21)**—**(29)** than in $[Ru(bipy)_3]^{2+}$. This indicates an increase in separation of the energy levels of the metal *d* and ligand π^* orbitals. Since the same orbitals are well known[1] to be involved in the redox processes this is also reflected in an increase in the $\Delta E_{ox\text{-}red}$ values (Table 4). Furthermore, it appears that this increase results from both a lowering of the energy of the metal *d* orbitals, as shown by the increase in oxidation potentials, and a raising of the level of the ligand π^* orbitals, as shown by the increase in reduction potentials.

For series of complexes of the type $[Ru(bipy)_{3-x}(L–L')_x]^{2+}$ plots of oxidation potentials *versus* *x* have recently[48] been shown to produce straight lines for a wide range of ligands L–L'. The slopes of such plots were used to derive ligand parameters P_L which were correlated to the π-donor/π-acceptor properties of the ligand.[48] For the present series of complexes plots of E_{ox} *versus* *x* gave straight lines and derived ligand parameters P_L: **(1)**, −1.13; **(2)**, −1.07; **(5)**, −1.09; **(9)**, −1.06. Thus, in accord with the conclusions drawn from the n.m.r. spectra, the ligands **(2)** and **(5)** are each better π acceptors than is the parent ligand **(1)**.

Conclusion

With the exception of the benzoxazole **(10)** the new pyrazole-containing ligands **(2)**—**(9)** have been shown readily to form stable complexes with ruthenium(II). Despite the complexity of many of the spectra it has been possible fully to assign all the ^{1}H and ^{13}C n.m.r. spectra of these complexes. The derived co-ordination-induced shift values have been shown to provide useful structural and bonding information which complements that obtained from absorption spectroscopy and electrochemi-

Table 5. Experimental details for the preparations of the complexes $[Ru(bipy)_2(L\text{–}L')][PF_6]_2$ and $[Ru(L\text{–}L')_3][PF_6]_2$

Complex	Yield/%	Colour	Analysis*/% C	H	N
(11)	81	Orange	39.5 (39.6)	2.7 (2.7)	11.6 (11.6)
(12)	82	Orange	38.0 (38.2)	2.6 (2.6)	12.8 (13.2)
(13)	72	Red	37.8 (38.2)	2.6 (2.6)	12.9 (13.2)
(14)	80	Red	38.3 (38.2)	2.6 (2.6)	13.1 (13.2)
(15)	97	Orange	38.5 (38.2)	2.6 (2.6)	13.2 (13.2)
(16)	89	Red	42.5 (42.8)	2.8 (2.8)	10.8 (10.9)
(17)	67	Orange	36.4 (36.5)	2.4 (2.5)	11.3 (11.5)
(18)	94	Orange	36.6 (36.5)	2.7 (2.5)	11.3 (11.5)
(19)·CD_3CN	86	Orange	40.4 (40.5)	2.7 (2.8)	11.7 (11.8)
(21)	85	Yellow	34.7 (34.9)	2.7 (2.6)	15.1 (15.3)
(22)·$0.5H_2O$	85	Yellow	30.1 (30.1)	2.1 (2.3)	19.6 (20.0)
(23)·$0.5H_2O$	66	Black	30.1 (30.1)	2.3 (2.3)	19.7 (20.0)
(24)·0.5EtOH	49	Red	30.8 (31.0)	2.6 (2.5)	19.6 (19.7)
(25)·0.5EtOH	50	Brown	31.5 (31.0)	2.7 (2.5)	19.8 (19.7)
(29)·$2H_2O$	87	Yellow	34.9 (34.9)	2.4 (2.4)	12.0 (12.2)

* Calculated values in parentheses.

cal measurements. Replacement of the pyridine ring in ligand (**1**) by other nitrogen-containing heterocycles is found to modify the properties of the resulting complexes in a predictable manner. These new ligands therefore further extend the range of ligand properties available for tuning the ground- and excited-state properties of transition-metal complexes for use as electrocatalysts and photosensitisers.

Experimental

Proton and ^{13}C n.m.r. spectra were recorded with a Bruker AM400 spectrometer on CD_3CN solutions, u.v.–visible absorption spectra using a Uvikon 810 spectrophotometer and CH_3CN solutions. Redox potentials were determined by using a Princeton Applied Research model 170 electrochemistry system; doubly distilled (from P_2O_5 then CaH_2) acetonitrile was used as solvent with *ca.* 0.1 mol dm^{-3} $[NBu_4][BF_4]$ as supporting electrolyte. Platinum beads were used as working and auxiliary electrodes with a silver wire as reference electrode; all measurements were carried out with ferrocene as internal standard, and potentials are given *versus* the saturated calomel electrode (s.c.e.) by normalising $[Ru(bipy)_3]^{2+}$ at 1.26 V. The compounds $[Ru(bipy)_2Cl_2]$ and $[Ru(dmso)_4Cl_2]$ were prepared by the literature procedures[49,50] from commercial $RuCl_3 \cdot xH_2O$. The ligands (**1**)—(**10**) were prepared as previously reported.[28,51]

Procedures for the Preparation of Co-ordination Compounds.—(*a*) $[Ru(bipy)_2(L\text{–}L')][PF_6]_2$ (**11**)—(**19**). The compound $[Ru(bipy)_2Cl_2]$ (0.2 mmol) was refluxed in ethanol–water (3:1) solution for 1 h. The ligand L–L′ (0.22 mmol) was then added and the resulting solution refluxed for 4—6 h. The mixture was cooled (and if necessary filtered to remove excess of unreacted ligand) then concentrated to dryness under reduced pressure. The residue was dissolved in water (*ca.* 20 cm^3) and the product was then precipitated by the dropwise addition of an aqueous solution of NH_4PF_6. The complex was then recrystallised from either ethanol–water or by slow diffusion of diethyl ether into an acetonitrile solution of the complex. Specific details for the individual complexes (**11**)—(**19**) are given in Table 5.

The ^1H n.m.r. spectra (400 MHz) for compound (**1**) and complex (**11**) recorded in $(CD_3)_2SO$ are as follows: (**1**), δ 7.823, $H^{3'}$; 6.571, $H^{4'}$; 8.620, $H^{5'}$; 7.928, H_b; 7.984, H_c; 7.343, H_d; 8.464, H_e; (**11**), δ 7.556, $H^{3'}$; 6.947, $H^{4'}$; 9.361, $H^{5'}$; 8.465, H_b; 8.231, H_c; 7.392, H_d; 7.592, H_e; 8.832 (3 H, 8.801, bipy H^3); 8.190 (2 H), 8.171; 8.140, bipy H^4; 7.592, 7.545, 7.530, 7.484, bipy H^5; 7.924, 7.816, 7.764, 7.725, bipy H^6.

Reaction of ligand (**10**) as above gave in 60% yield a product identified as $[Ru(bipy)_2(Hpz)Cl]PF_6 \cdot 0.5EtOH$ (Found: C, 42.3; H, 3.2; N, 12.1. $C_{23}H_{20}ClF_6N_6OPRu \cdot 0.5C_2H_6O$ requires C, 42.2; H, 3.4; N, 12.3%). ^1H N.m.r. (CD_3CN, 400 MHz): δ 7.765, pz H^3; 6.297, pz H^4; 6.509, pz H^5; 8.466, 8.399, 8.350, 8.336, bipy H^3; 8.055, 8.044, 7.847, 7.830, bipy H^4; 7.685, 7.564, 7.207, 7.184, bipy H^5; 9.891, 8.174, 7.816, 7.680, bipy H^6.

(*b*) $[Ru(L\text{–}L')_3][PF_6]_2$ (**21**)—(**29**). A solution of $[Ru(dmso)_4Cl_2]$ (0.2 mmol) and the ligand L–L′ (0.66 mmol) in ethanol–water (3:1) (20 cm^3) was refluxed for 16—20 h. The solution was cooled (and if necessary filtered to remove excess of unreacted ligand) then concentrated to *ca.* 6 cm^3 under reduced pressure. Water (*ca.* 10 cm^3) was added and the product was then precipitated by dropwise addition of an aqueous solution of NH_4PF_6. In the case of the complex (**27**) cooling was necessary to induce separation of the product. The complex was then recrystallised from either ethanol–water or by slow diffusion of diethyl ether into an acetonitrile solution of the complex. Specific details for the individual complexes (**21**)—(**29**) are given in Table 5.

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