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Syntheses of Chelating Tetrazole-Containing Ligands and Studies of Their Palladium(II) and Ruthenium(II) Complexes

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Abstract

Eleven chelating tetrazole-containing ligands have been synthesized, and their complexes with palladium(II) and ruthenium(II) prepared. Proton n.m.r. spectroscopy, electronic absorption spectroscopy and cyclic voltammetry have been used to study the nature of the metal–ligand interactions in these complexes. The negatively charged tetrazolate group is shown to be a strong electron donor with very different properties to those of the protonated or alkylated tetrazole group. This leads to pH control of the properties of transition metal complexes containing such ligands.

Introduction

Aromatic nitrogen heterocycles represent an important class of ligand for transition metal coordination chemistry.[1] The major division in the classification of aromatic nitrogen heterocycles is according to ring size. The six-membered ring nitrogen heterocycles (azines, e.g. pyridine) are π-deficient with relatively low energy π^* orbitals which allow good metal–ligand back-bonding from the d-orbitals of the metal to the π-system of the ligand. The five-membered aromatic nitrogen heterocycles (azoles), on the other hand, are π-excessive π-donors and can also form anionic ligands by deprotonation of acidic NH groups in the free ligand. Heterocycles with more than one nitrogen atom in six-membered (diazines, triazines, etc.) rings and five-membered (diazoles, triazoles, etc.) rings are also useful as ligands, and have quite different electronic properties to those of pyridine. In addition, they possess multiple coordination sites and are therefore potentially capable of bridging more than one metal centre.

The most well studied chelating heterocyclic ligand is 2,2′-bipyridine (bpy). This ligand was first synthesized over 100 years ago,[2] and has been extensively used in preparative and analytical coordination chemistry because of the stable bidentate complexes it forms with most transition metals.[3] In recent years, many bidentate chelating ligands related to bpy have been synthesized in which one or both of the pyridine rings are replaced with either azines or azoles.[4]

[1] Reedijk, J., in 'Comprehensive Coordination Chemistry' (Eds G. Wilkinson, R. D. Gillard and J. A. McCleverty) Vol. 2, p. 73 (Pergamon: Oxford 1987).
[2] Blau, F., *Ber. Dtsch. Chem. Ges.*, 1888, **27**, 1077.
[3] Constable, E. C., *Adv. Inorg. Chem.*, 1989, **34**, 1.
[4] Constable, E. C., and Steel, P. J., *Coord. Chem. Rev.*, 1989, **93**, 205.

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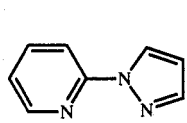
These ligands form complexes with properties which depend markedly on the specific heterocycles incorporated. Thus, by the appropriate choice of ligand, it is possible to tune, in a predictable manner, the ground and excited state properties of complexes such as in the well studied $Ru(bpy)_3^{2+}$ complex.[5]

There have been several recent studies of the metal complexes of 2-(*N*-pyrazolyl)pyridine (1) with particular emphasis on its ruthenium(II) complexes.[6] Replacement of one of the pyridine rings of bpy by a pyrazole ring, as in (1), results in significant changes in the physicochemical properties of the complexes. Similarly, there have been many recent reports of ruthenium(II) and osmium(II) complexes of chelating ligands containing triazole rings, e.g. 2-(1,2,4-triazol-3-yl)pyridine (2).[7] Again the triazole ring alters the properties of the complexes but in this case the presence of the acidic NH proton allows pH control of the properties of the complexes since the protonated and deprotonated forms of the ligand have very different electronic properties.[7] Furthermore, the deprotonated triazole ring has more than one nitrogen available for coordination, and such ligands can lead to the formation of binuclear complexes.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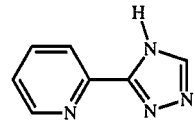
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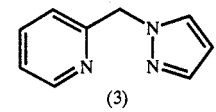

(3)

A number of bidentate and tridentate ligands have recently been described in which the heterocyclic rings have been separated by a methylene group. Examples of such ligands include 2-(*N*-pyrazolylmethyl)pyridine (3),[8] 6-(*N*-pyrazolylmethyl)-2,2′-bipyridine[9] and 2,6-bis(*N*-pyrazolylmethyl)pyridine.[10] The introduction of such methylene groups results in the formation of six-membered chelate rings on coordination to a metal, rather than five-membered chelate rings. This changes the bite angle of the ligand and introduces conformational flexibility, since such six-membered chelate rings exist in boat conformations.[11] In addition, the

[5] Juris, A., Balzani, V., Barigelletti, F., Campagna, S., Belser, P., and von Zelewsky, A., *Coord. Chem. Rev.*, 1988, **84**, 85, and references therein.

[6] Steel, P. J., Lahousse, F., Lerner, D., and Marzin, C., *Inorg. Chem.*, 1983, **22**, 1488; Hage, R., Prins, R., Haasnoot, J. G., Reedijk, J., and Vos, J. G., *J. Chem. Soc., Dalton Trans.*, 1987, 1389; Baker, A. T., Ferguson, N. J., Goodwin, H. A., and Rae, A. D., *Aust. J. Chem.*, 1989, **42**, 623; Steel, P. J., and Constable, E. C., *J. Chem. Soc., Dalton Trans.*, 1990, 1389.

[7] Hage, R., Haasnoot, J. G., Nieuwenhuis, H. A., Reedijk, J., Wang, R., and Vos, J. G., *J. Chem. Soc., Dalton Trans.*, 1991, 3271; Buchanan, B. E., Degn, P., Velasco, J. M. P., Hughes, H., Creaven, B. S., Long, C., Vos, J. G., Howie, R. A., Hage, R., van Dieman, J. H., Haasnoot, J. G., and Reedijk, J., *J. Chem. Soc., Dalton Trans.*, 1992, 1177.

[8] House, D. A., Steel, P. J., and Watson, A. A., *Aust. J. Chem.*, 1986, **39**, 1525; Byers, P. K., Canty, A. J., Honeyman, R. T., and Watson, A. A., *J. Organomet. Chem.*, 1990, **385**, 429.

[9] Downard, A. J., Honey, G. E., and Steel, P. J., *Inorg. Chem.*, 1991, **30**, 3733.

[10] House, D. A., Steel, P. J., and Watson, A. A., *Inorg. Chim. Acta*, 1987, **130**, 167; Mahapatra, S., Gupta, N., and Mukherjee, R., *J. Chem. Soc., Dalton Trans.*, 1991, 2911; Mahapatra, S., and Mukherjee, R., *J. Chem. Soc., Dalton Trans.*, 1992, 2337; Mahapatra, S., Lal, T. K., and Mukherjee, R. N., *Polyhedron*, 1993, **12**, 1477; Mahapatra, S., and Mukherjee, R. N., *Polyhedron*, 1993, **12**, 1603.

[11] Joshi, V. S., Sarkar, A., and Rajamohanan, P. R., *J. Organomet. Chem.*, 1991, **409**, 341, and references therein; Shiu, K.-B., Liou, K.-S., Wang, Y., Cheng, M.-C., and Lee, G.-H., *J. Organomet. Chem.*, 1993, **453**, 201.

methylene group prevents the possibility of conjugation between the component heterocyclic rings. For example, whereas there is extensive conjugation between the π-excessive pyrazole and the π-deficient pyridine rings in (1), this is not possible in the case of (3).

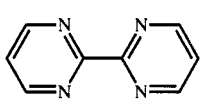
Another area that has attracted much interest in recent years is that of binucleating heterocyclic ligands.[12] For example, ligands such as 2,2′-bipyrimidine (4),[13] 2,3-bis(2-pyridyl)pyrazine[14] and 2,2′:4′,4″:2″,2‴-quaterpyridine[15] are each capable of chelating to two metal centres. In these binuclear complexes there exists the possibility of metal–metal interactions, such as energy or electron transfer, magnetic coupling and intervalence transfer. These interactions are mediated by the bridging ligand, with communication between the metal centres generally taking place via the π-system of the ligand. It is possible to control the extent of such interactions by varying the metal–metal distance, the extent of conjugation between the coordination sites, and the charge and π-donor/acceptor properties of the ligand used to bridge the metals.

The present work describes the preparations and complexes of new heterocyclic ligands which incorporate tetrazole rings. Tetrazole (5) is the most acidic of all the azoles ($pK_a = 4{\cdot}89$)[16] and readily deprotonates to the tetrazolate ion (6). Incorporation of a tetrazole ring into a chelating ligand is possible by attachment through either the tetrazole carbon (C 5) or either of the two non-equivalent nitrogens (N 1 or N 2). Thus three possible isomers can exist for chelating ligands containing one tetrazole ring, and a fourth ligand can be produced by deprotonation of a C 5 substituted tetrazole. Complexes of these different isomers are likely to have significantly different properties, since it is well known that *C*-substituted tetrazoles have different electronic characteristics from *N*-substituted tetrazoles. For example the Hammett σ_I values for tetrazol-5-yl, tetrazol-1-yl, tetrazol-2-yl and tetrazol-5-ato groups are 0·45, 0·69, 0·62 and 0·12 respectively.[17] If the attached heterocycle contains two suitably located nitrogens, a 5-substituted tetrazolate ligand can also act in a binucleating mode. This has the advantage, over ligands such as 2,2′-bipyrimidine, that the ligand is anionic and should therefore form more stable binuclear complexes by reducing repulsion between the positively charged metal centres.[18]

Preliminary studies of the coordination chemistry of the new chelating ligands described below were undertaken. For this purpose, palladium(II) and ruthenium(II) complexes were selected for study because of the abundance of spectroscopic and electrochemical literature data for structurally related compounds. For example, a recent review[5] surveyed the properties of the ruthenium(II) complexes of over 250 heterocyclic ligands. However, none of these ligands contained tetrazole groups. Indeed the coordination chemistry of tetrazoles has received surprisingly little attention in the past. In 1977, a review[19] of the chemistry of tetrazoles

[12] Steel, P. J., *Coord. Chem. Rev.*, 1990, **106**, 227.
[13] Krejcik, M., and Vlcek, A. A., *Inorg. Chem.*, 1992, **31**, 2390, and references therein.
[14] Richter, M. M., and Brewer, K. J., *Inorg. Chem.*, 1992, **31**, 1594, and references therein.
[15] Downard, A. J., Honey, G. E., Phillips, L. F., and Steel, P. J., *Inorg. Chem.*, 1991, **30**, 2260.
[16] Katritzky, A. R., 'Handbook of Heterocyclic Chemistry' p. 303 (Pergamon: Oxford 1985).
[17] Mamaev, V. P., Shkurko, O. P., and Baram, S. G., *Adv. Heterocycl. Chem.*, 1987, **42**, 1.
[18] Haga, M., Matsumura-Inoue, T., and Yamabe, S., *Inorg. Chem.*, 1987, **26**, 4148.
[19] Butler, R. N., *Adv. Heterocycl. Chem.*, 1977, **21**, 323.

discussed the metal complexes of tetrazoles such as the parent compound (5), 5-phenyltetrazole and 1,5-disubstituted derivatives. Such ligands are only capable of monodentate coordination to a metal centre and, as such, the complexes are less stable than the corresponding complexes of the chelating ligands described below. In 1979 the first complexes of chelating tetrazole-containing ligands were described.[20] Infrared and ultraviolet–visible spectra, magnetic moments and X-ray diffraction patterns were used to characterize the first row transition metal complexes of 5-(2-pyridyl)tetrazole (7). Subsequently,[21] a palladium(II) complex of the deprotonated form of (7) was prepared by a 1,3-cycloaddition reaction of $(Ph_3P)_2Pd(N_3)_2$ with pyridine-2-carbonitrile. In 1988 a full review of the coordination chemistry of tetrazoles and tetrazolates was published.[22] This did not include any new chelating heterocycle-containing ligands.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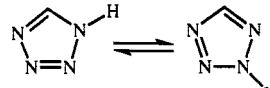
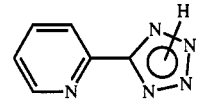
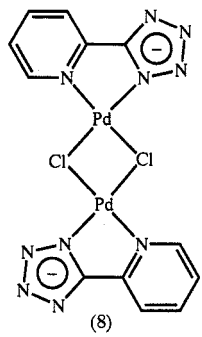

(5a) (5b)


(6)


(7)

Results and Discussion

The first ligand to be investigated was 5-(2-pyridyl)tetrazole (Hpyt) (7). This can be prepared by reaction of pyridine-2-carbonitrile and hydrazoic acid, and is commercially available. Reaction of (7) with 1 equiv. of palladium(II) dichloride in 2 M hydrochloric acid gave, in good yield, a yellow complex, which was shown by elemental analysis to be the chloro-bridged dimer $Pd_2(pyt)_2Cl_2$ (8), rather than the protonated mononuclear complex $Pd(Hpyt)Cl_2$. This complex was insoluble in all common solvents and was not further investigated. Reaction of (7) with 1 equiv. of bis(2,2′-bipyridine)dichlororuthenium(II) in 1 : 2 water/ethanol afforded in reasonable yield the complex $Ru(bpy)_2(pyt)^+$ (9) which was isolated as the hexafluorophosphate salt and characterized by elemental analysis. Thus, in both cases, the ligand Hpyt (7) formed complexes as the deprotonated tetrazolate form. This is consistent with the high acidity of the NH proton in tetrazoles.[16]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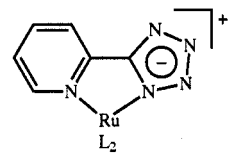
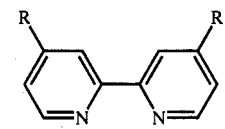

(9) L = bpy
(10) L = dmb


bpy R = H
dmb R = Me

[20] Gill, N. S., and Yang, F. Y., *Aust. J. Chem.*, 1979, **32**, 1669.
[21] Erbe, J., and Beck, W., *Chem. Ber.*, 1983, **116**, 3867.
[22] Moore, D. S., and Robinson, S. D., *Adv. Inorg. Chem.*, 1988, **32**, 171.

The ^{1}H n.m.r. spectrum of (9) in (D_3)acetonitrile shows 20 non-equivalent protons (five 2-substituted pyridine rings) due to the unsymmetrical nature of the pyt ligand. Despite considerable overlap of these signals, the five protons H6 are all resolved from each other in the region 7·6–8·0 ppm. A two-dimensional ^{1}H–^{1}H correlated spectrum (COSY) facilitated additional assignments of some of the other proton signals, but did not allow a complete assignment of the entire spectrum, due to the significant overlap of the H3 and H4 signals. Isolation of the five individual four-proton spin systems was achieved by means of a series of one-dimensional TOCSY[23,24] experiments. This technique is particularly useful for the isolation of individual spin systems in highly overlapping spectra, as it requires only one non-overlapping proton for each spin system.[24] The four signals of each pyridine ring were located by this technique for each of the five pyridine rings. Nevertheless, this does not locate the stereochemical environment of each individual pyridine ring within the complex. In fact, the signals for the pyt ligand could not be identified with certainty.

This was achieved by differentiating the bpy pyridine rings from the pyt pyridine ring through their replacement with 4,4′-dimethyl-2,2′-bipyridine (dmb) ligands. Thus, reaction of Hpyt (7) with 1 equiv. of $Ru(dmb)_2Cl_2$ gave the complex $Ru(dmb)_2(pyt)^+$ (10) as the PF_6 salt in 84% yield. This considerably simplified the ^{1}H n.m.r. spectrum. Specifically, four of the overlapping protons H4 at *c.* 8·0 ppm in the spectrum of (9) disappeared (being replaced by four methyl signals at *c.* 2·6 ppm). Furthermore, all ^3J and ^4J couplings involving H4 are removed in the spectrum of the dmb substituted complex (10). An alternative procedure has previously been described for simplifying similar overlapping ^{1}H n.m.r. spectra of ruthenium(II) complexes.[25] This involves using fully deuterated bpy ligands ((D_8)bpy), thereby completely eliminating the bpy signals. However, aside from the excessive cost of (D_8)bpy, this technique sacrifices the information contained in the chemical shifts of the bpy protons.

Table 1 summarizes the n.m.r. data for Hpyt and its ruthenium complexes in CD_3CN, and includes the coordination-induced shift values (CIS = $\delta_{complex} - \delta_{ligand}$). Some dramatic upfield shifts are observed for the pyt pyridine proton signals on coordination to ruthenium. Previously, a number of factors have been identified that contribute to the sign and magnitude of the CIS values in such ruthenium(II) complexes[9,26] (see also Steel and Constable[6]). Ligand-to-metal σ donation, metal-to-ligand π back donation, chelation-imposed conformational changes, coordinative disruption of inter-ring conjugation and interligand through-space ring-current anisotropy effects have all been invoked to explain CIS values of tris(biheteroaromatic)ruthenium(II) complexes. In the present case all four protons of the pyridine ring of Hpyt are shifted upfield on coordination to ruthenium. By far the largest upfield CIS (−1·17 ppm) is experienced by H6. This is undoubtedly due to through-space ring-current anisotropy effects since this proton lies directly over the shielding plane of one of the bpy (or dmb) pyridine rings. The other protons experience smaller upfield shifts (from −0·07 to −0·32 ppm)

[23] Kessler, H., Mronga, S., and Gemmecker, G., *Magn. Reson. Chem.*, 1991, **29**, 527.
[24] Braunschweiler, L., and Ernst, R. R., *J. Magn. Reson.*, 1983, **53**, 521; Davis, D. G., and Bax, A., *J. Am. Chem. Soc.*, 1984, **107**, 7197.
[25] Chirayil, S., and Thummel, R. P., *Inorg. Chem.*, 1989, **29**, 813.
[26] Orellana, G., Ibarra, C. A., and Santoro, J., *Inorg. Chem.*, 1988, **27**, 1025.

Table 1. ^{1}H n.m.r. chemical shifts and for (7), (9) and (10) in CD_3CN solutions

	H3	H4	H5	H6
(9)	8·538	8·023	7·444	7·954
	8·514	8·047	7·444	7·921
	8·488	8·047	7·425	7·815
	8·488	8·047	7·379	7·691
	8·344	8·022	7·306	7·620
(10) (dmb)	8·377	2·580[B]	7·270	7·748
	8·352	5·573[B]	7·252	7·707
	8·332	2·563[B]	7·234	7·665
	8·332	2·563[B]	7·213	7·489
(pyt)	8·318	7·990	7·282	7·618
(7)	8·311	8·056	7·603	8·794
CIS[A]	0·007	−0·066	−0·321	−1·176

[A] CIS = $\delta_{complex} - \delta_{ligand}$. [B] Methyl groups.

due to a combination of factors. Negative CIS values are usually ascribed to strong metal-to-ligand π back donation; however, in the present case they may simply be a consequence of deprotonation of the tetrazole and the resulting transfer of electron density from the negatively charged tetrazolate ring to the π-deficient pyridine ring. This possibility can be probed by ultraviolet–visible absorption spectroscopy and electrochemical measurements.

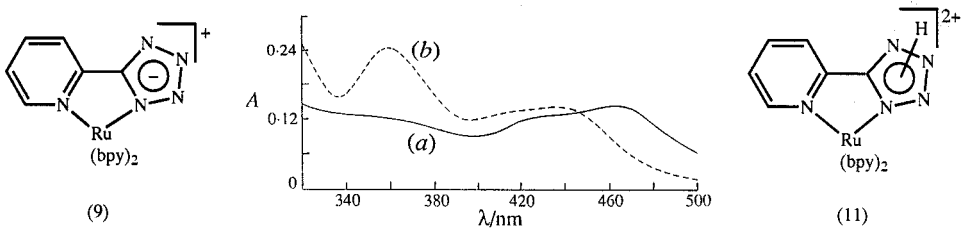


Fig. 1. Ultraviolet–visible spectrum of (9) in acetonitrile: (*a*) without acid; (*b*) with added acid.

Fig. 1 shows the electronic absorption spectrum of complex (9) with and without added acid. Addition of acid converts the tetrazolate complex $Ru(bpy)_2(pyt)^+$ (9) into the tetrazole complex $Ru(bpy)_2(Hpyt)^{2+}$ (11). The spectra consist of strong ligand-centred absorptions at $\lambda < 300$ nm and MLCT absorptions at $\lambda > 400$ nm. The complex (9) absorbs at lower energy (466 nm) than $Ru(bpy)_3^{2+}$ (451 nm).[27] This means that electron transfer from the metal to one of the ligands of (9) requires less energy than in the case of $Ru(bpy)_3^{2+}$. Addition of acid, however, moves the MLCT absorption to higher energy (436 nm) than that of $Ru(bpy)_3^{2+}$. The corresponding values for the dmb complex (10) are 459 nm (without acid) and

[27] Belser, P., and von Zelewsky, A., *Helv. Chim. Acta*, 1980, **63**, 1675.

428 nm (with acid). Such pH control of the physical properties of ruthenium(II) complexes has recently been shown to have important consequences.[28]

Further insight into these effects is provided by electrochemical data. Fig. 2 shows the cyclic voltammograms of $Ru(bpy)_2(pyt)^+$ (9) and, after addition of acid, $Ru(bpy)_2(Hpyt)^{2+}$ (11). The tetrazolate complex (9) exhibits a reversible one-electron oxidation at $E^{\circ\prime} = +1{\cdot}02$ V and two reversible one-electron reductions at $E^{\circ\prime} = -1{\cdot}50$ and $-1{\cdot}72$ V. There are no other reductions within the solvent limit. Thus relative to $Ru(bpy)_3^{2+}$ ($E^{\circ\prime} = +1{\cdot}27$, $-1{\cdot}31$, $-1{\cdot}50$, $-1{\cdot}77$ V *v.* s.c.e.)[5] the complex (9) is more easily oxidized but more difficult to reduce. Clearly the negatively charged tetrazolate group is a powerful electron donor which significantly increases the electron density at the ruthenium centre. Furthermore, the ΔE_{ox-red} value (2·52 V) is less than that of $Ru(bpy)_3^{2+}$ (2·58 V), consistent with the visible absorption spectra for which the same orbitals are involved.[5] Addition of acid results in a significant increase in the oxidation potential ($E^{\circ\prime} = +1{\cdot}17$ V) for the dication (11), relative to the monocation (9), and this is consistent with the shift to higher energy of the MLCT absorption. Access to the reduction potentials of (11) was prevented by reduction of excess acid to hydrogen.

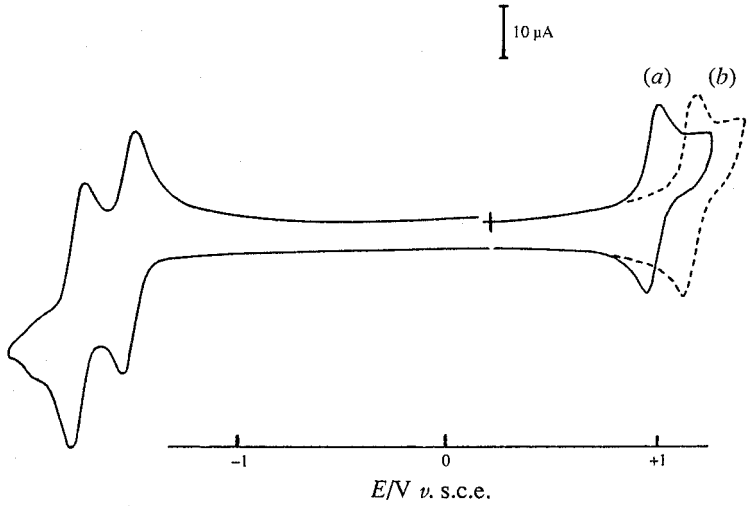


Fig. 2. Cyclic voltammograms of (9) recorded in acetonitrile (scan rate 100 mV s^{-1}): (*a*) without acid; (*b*) with added acid.

For the dmb complex (10) reversible oxidation occurs at $E^{\circ\prime} = +0{\cdot}91$ V and reversible reductions occur at $E^{\circ\prime} = -1{\cdot}61$ and $-1{\cdot}84$ V. Thus, introduction of the four electron-donating methyl groups into the bpy ligands increases the ease of oxidation by 0·11 V. It has been previously noted for structurally related compounds that methyl groups decrease oxidation potentials by approximately 0·025 V per methyl group.[29] These results are summarized in Table 2.

[28] Nieuwenhuis, H. A., Haasnoot, J. G., Hage, R., Reedijk, J., Snoeck, T. L., Stufkens, D. J., and Vos, J. G., *Inorg. Chem.*, 1991, **30**, 48; Wang, R., Vos. J. G., Schmehl, R. H., and Hage, R., *J. Am. Chem. Soc.*, 1992, **114**, 1964.

[29] Jameson, D. L., Blaho, J. K., Kruger, K. T., and Goldsby, K. A., *Inorg. Chem.*, 1989, **28**, 4312.

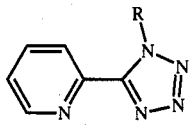
Table 2. Visible absorption maxima (in nm) and redox potentials (in V *v.* s.c.e.) measured in acetonitrile

Complex	λ_{max}	$E^{\circ\prime}_{ox}$	$E^{\circ\prime}_{red(1)}$	$E^{\circ\prime}_{red(2)}$	$E^{\circ\prime}_{red(3)}$	$\Delta E_{ox-red(1)}$
$Ru(bpy)_3^{2+}$	451	+1·27	−1·31	−1·50	−1·77	2·58
(9)	466	+1·02	−1·50	−1·72	[A]	2·52
(10)	459	+0·91	−1·61	−1·84	[A]	2·52
(18)	423	+1·33	−1·37	−1·59	−1·82	2·70
(19)	424	+1·31	−1·42	−1·61	−1·95	2·73
(20)	423	+1·29	−1·43	−1·65	−1·99	2·72

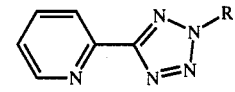
[A] Not observed.

In order to simplify the complications associated with the acidity of the tetrazole proton and the resulting pH dependence of the properties of the complexes, it was decided to methylate the tetrazole ring of Hpyt, since a methyl group cannot be lost on complexation. Methylation of (7) can give two possible products, 1-methyl-5-(2-pyridyl)tetrazole (12) and 2-methyl-5-(2-pyridyl)tetrazole (13).[30] Methylation with methyl iodide and sodium hydroxide in refluxing ethanol/water[31] gave a mixture of (12) and (13) in a 1:1 ratio in 48% combined yield. Despite several attempts to separate these isomers only partial separation was achieved by careful radial chromatography. Alternative methods of methylation were investigated. Reaction with methyl iodide and potassium carbonate in acetonitrile[32] afforded a 2:3 ratio of (12) and (13) in 73% combined yield. Reaction of (7) with methyl iodide in refluxing acetone[33] gave a 3:7 ratio of (12) and (13) in 76% yield. In this case the major isomer (13) crystallized from the mixture and the minor isomer (12) was recrystallized from the residue. These two isomers were characterized by ^{1}H n.m.r. and ^{13}C n.m.r., and tentatively distinguished from one another on the basis that the methyl protons of the 2-methyl isomer resonate downfield of those of the 1-methyl isomer for structurally related compounds[31] (see also Spear[33]). However, a subsequent X-ray structure determination of (12) has since revealed that this criterion does not apply to these isomers.

In an attempt to effect totally selective alkylation, t-butylation reactions were carried out, since these might be expected to be more regioselective. Reaction of (7) with t-butyl alcohol in the presence of dicyclohexylcarbodiimide and



(12) R = Me
(14) R = Bu^t

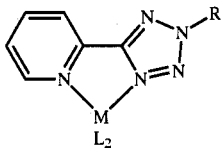


(13) R = Me
(15) R = Bu^t

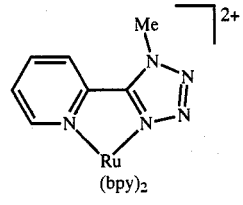
[30] Benjes, P. A., and Grimmett, M. R., 'Advances in Detailed Reaction Mechanisms' (Ed. J. M. Coxon) Vol. 3, p. 199 (JAI: Greenwich, Connecticut, 1994).
[31] Butler, R. N., Garvin, V. C., and McEvoy, T. M., *J. Chem. Res.*, 1981, 174; *J. Chem. Soc., Perkin Trans. 1*, 1981, 390.
[32] Katritzky, A. R., Kuzmierkiewicz, W., and Greenhill, J. V., *Recl Trav. Chim. Pays-Bas*, 1991, **110**, 369.
[33] Holland, G. F., and Pereira, J. N., *J. Med. Chem.*, 1967, **10**, 149; Spear, R. J., *Aust. J. Chem.*, 1984, **37**, 2453.

cuprous chloride[34] gave a 3:2 mixture of 1-t-butyl-5-(2-pyridyl)tetrazole (14) and 2-t-butyl-5-(2-pyridyl)tetrazole (15) in 72% yield. In contrast, alkylation by a recently reported[35] more regioselective procedure, with t-butyl alcohol in trifluoroacetic acid and concentrated sulfuric acid, gave exclusively the 2-butylated isomer (15) which was fully characterized by spectroscopic techniques.

Reactions of the alkylated tetrazoles (12), (13) and (15) with palladium(II) and ruthenium(II) were investigated. Reaction of 2-methyl-5-(2-pyridyl)tetrazole (13) with palladium(II) dichloride in 2 M hydrochloric acid gave, in 77% yield, a yellow complex which was shown by elemental analysis to be the mononuclear complex (16). This complex was soluble but slowly solvolysed in $(CD_3)_2SO$. Relative to the spectrum of the free ligand (13) in the same solvent, all five proton n.m.r. signals moved downfield in the complex (16). Specifically, the CIS values were +0·19 (H3′), +0·48 (H4′), +0·36 (H5′), +0·32 (H6′) and +0·14 (Me). These downfield shifts reflect the σ-donation of electron density from the ligand to the metal. Similarly, reaction of 2-t-butyl-5-(2-pyridyl)tetrazole (15) with $PdCl_2$ gave the mononuclear complex (17) which also decomposed in $(CD_3)_2SO$, and which exhibited similar downfield CIS values.



	R	ML_2
(16)	Me	$PdCl_2$
(17)	Bu^t	$PdCl_2$
(19)	Me	$Ru(bpy)_2^{2+}$
(20)	Bu^t	$Ru(bpy)_2^{2+}$



(18)

Reactions of (12), (13) and (15) with 1 equiv. of bis(2,2′-bipyridine)dichlororuthenium(II) in 1:2 water/ethanol afforded, in good yields, the corresponding dications (18), (19) and (20) which were isolated as the hexafluorophosphate salts, and characterized by elemental analyses. The proton n.m.r. spectra of these complexes again show 20 non-equivalent aromatic proton signals, corresponding to the five 2-substituted pyridine rings, along with the signals for the methyl (or t-butyl) groups. The CIS values are similar to those observed for the earlier complexes.

The ultraviolet–visible and electrochemical data for these complexes are also included in Table 2. These complexes all absorb at higher energy than the monocation (9) and are therefore more similar to the protonated form (11). Thus metal-to-ligand charge transfer requires more energy than in the deprotonated complex (9). The origin of this is revealed in the electrochemical data. Fig. 3 shows the cyclic voltammagram of the complex (19) in acetonitrile. This shows a reversible one-electron oxidation at $E^{\circ\prime} = 1{\cdot}31$ V and three reversible one-electron reductions at $E^{\circ\prime} = -1{\cdot}42$, $-1{\cdot}61$ and $-1{\cdot}95$ V. Relative to the deprotonated complex (9), the methylated complex (19) is considerably more difficult to oxidize but slightly more easily reduced. Thus the energy of the metal-based HOMO is lowered (by 0·29 eV) in the complex (19) and the bpy-based LUMO is lowered by only 0·09 eV. The HOMO–LUMO energy difference is therefore greater in (19), as

[34] Henry, R. A., *J. Heterocycl. Chem.*, 1976, **13**, 391.
[35] Kanno, H., Yamagushi, H., Ichikawa, Y., and Isoda, S., *Chem. Pharm. Bull.*, 1991, **39**, 1099.

is also reflected in the ultraviolet–visible absorption spectrum (Table 2). Indeed in all the complexes discussed so far there is a correlation between the MLCT absorption maxima and the ΔE_{ox-red} values as these involve the same molecular orbitals. As shown in Fig. 3 all three ligands undergo reversible reductions in the complex (19), whereas the deprotonated complex (9) showed only two reductions (Fig. 2). This is because one of the ligands in the complex (9) is negatively charged and therefore a much poorer electron acceptor.

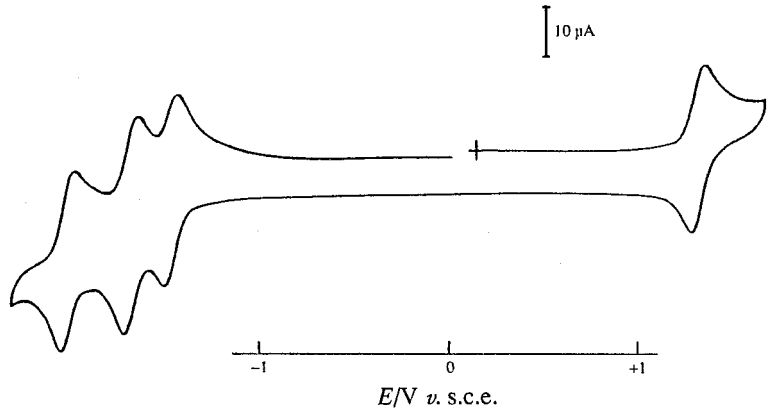


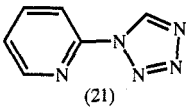
Fig. 3. Cyclic voltammogram of (19) recorded in acetonitrile (scan rate 100 mV s^{-1}).

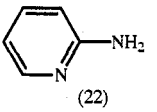
The bidentate ligands discussed thusfar all have the pyridyl rings attached to the carbon (C 5) of the tetrazole ring. It is well known that *C*-linked heterocycles have very different properties from *N*-linked heterocycles.[17,36] It was therefore decided to attempt the preparation of a C–N linked pyridyltetrazole. Several attempts at nucleophilic substitution of 2-bromopyridine by tetrazolate anion in various solvents for prolonged reaction times failed to produce useful amounts of either of the two possible isomers of an *N*-(2-pyridyl)tetrazole. Reaction of 2-bromopyridine with tetrazole, potassium carbonate and cupric oxide in refluxing pyridine, according to a literature procedure for the preparation of structurally related compounds,[37] gave a complex mixture of products in low yield. Chromatographic separation of this mixture resulted in the isolation of a very small amount of what was subsequently identified as 1-(2-pyridyl)tetrazole (21).

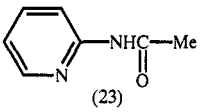
A more selective preparation of (21) was then attempted, based on a reported procedure for the preparation of 1-substituted tetrazoles by heterocyclization of primary amines with triethyl orthoformate and sodium azide.[38] However, reaction of 2-aminopyridine (22) with 1 equiv. of triethyl orthoformate and sodium azide in refluxing acetic acid gave *N*-(2-pyridyl)acetamide (23) as the major product, which was identified by comparison with an authentic sample prepared by reaction of (22) with acetic anhydride. 1-(2-Pyridyl)tetrazole (21) was finally prepared

[36] Karavai, V. P., Gaponik, P. N., and Ivashkevich, O. A., *Magn. Reson. Chem.*, 1989, **27**, 611.
[37] Khan, M. A., and Polya, J. B., *J. Chem. Soc. C*, 1970, 85.
[38] Gaponik, P. N., Karavai, V. P., and Grigor'ev, Y. V., *Khim. Geterotsikl. Soedin.*, 1985, 1521 (*Chem. Abstr.*, 1986, **105**, 60567m).

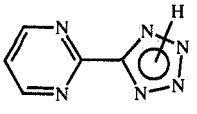
in good yield by reaction of (22) in acetic acid with a large excess of triethyl orthoformate. The structure was confirmed by mass spectrometry and ^{1}H n.m.r. comparison with related compounds. Attempts were then made to prepare palladium(II) and ruthenium(II) complexes of this new ligand. However, no such complexes could be structurally characterized. Elemental analyses suggested that this ligand readily loses molecular nitrogen. Tetrazoles are well known to lose nitrogen under a variety of conditions, often explosively.[39]

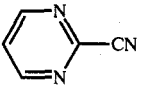

(21)

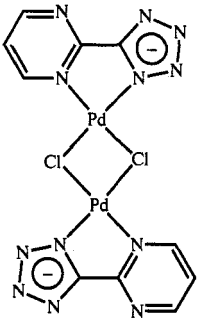

(22)


(23)

As descibed in the Introduction, there has been much interest in recent years in the study of binuclear complexes incorporating bridging heterocyclic ligands.[12] Of these ligands 2,2′-bipyrimidine (4) is by far the most well studied.[13] Replacement of one of the pyrimidine rings in (4) by a tetrazole ring is represented by the ligand 5-(pyrimidin-2-yl)tetrazole (24). Deprotonation of this potentially binucleating compound would give an anionic ligand which should lead to more stable binuclear complexes than those of (4) by reducing the repulsion between positively charged metal centres.[12,18] 5-(Pyrimidin-2-yl)tetrazole (24) was prepared in 50% yield by reaction of pyrimidine-2-carbonitrile (25) with sodium azide in refluxing acetic acid/isopropyl alcohol for 4 days. The ligand was characterized by mass spectrometry and ^{1}H n.m.r. Reaction of (24) with 1 equiv. of $PdCl_2$ afforded a chloro-bridged dimer (26) of the deprotonated form of (24). In this complex the ligand acts in a mononucleating mode. All attempts to prepare a binuclear complex by reaction with 2 equiv. of $PdCl_2$ resulted only in formation of the same complex (26). Reaction of (24) with $Ru(dmb)_2Cl_2$ followed by isolation of the hexafluorophosphate salts gave a product which was shown by ^{1}H n.m.r. to be a complex mixture of both mononuclear and binuclear compounds. As this mixture was not readily separable, no further studies were carried out on these complexes.


(24)

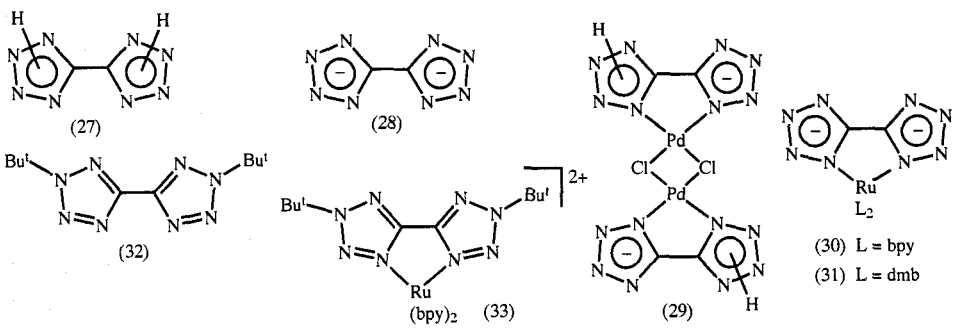

(25)


(26)

[39] Benson, F. R., *Chem. Rev.*, 1947, **41**, 1; Butler, R. N., *Adv. Heterocycl. Chem.*, 1977, **21**, 323.

Another potentially binucleating ligand is the known compound 5,5′-bitetrazole (27). This ligand was first prepared in 1922,[40] but an improved procedure for its preparation has recently been reported.[41] The first and second pK_a values for this compound have been measured as 1·41 and 4·25 respectively.[42] Thus double deprotonation of this ligand would produce the binucleating dianion (28).

5,5′-Bitetrazole (27) was prepared in 61% yield by the more recent literature procedure. Reaction with palladium chloride gave, in 60% yield, a complex which elemental analysis showed to be a chloro-bridged dimer (29) of the singly deprotonated ligand. This complex was insoluble in common organic solvents. Reaction of (27) with $Ru(bpy)_2Cl_2$ and $Ru(dmb)_2Cl_2$ gave products with ^1H n.m.r. spectra consistent with the structures of the neutral complexes (30) and (31) obtained from the doubly deprotonated ligand. These spectra are considerably less complicated than the spectra of the earlier ruthenium complexes because of the symmetrical nature of the bitetrazole ligand. In particular each of the two auxiliary ligands (bpy or dmb) are equivalent in each complex because of the presence of a twofold axis of symmetry. Nevertheless these complexes were not obtained in pure form because of contamination by binuclear impurities. Attempts to use them to prepare binuclear complexes have thus far not succeeded.



To prevent the formation of complexes of mixed nuclearity it was decided to alkylate the ligand (27). Since methylation would be expected to yield a mixture of three isomers, the more regioselective t-butylation procedure was carried out. Thus reaction of (27) with t-butyl alcohol in the presence of trifluoroacetic acid and sulfuric acid gave 2,2′-di-t-butyl-5,5′-bitetrazole (32) in 78% yield, and which was characterized by ^1H n.m.r. and mass spectrometry. Reaction of (32) with palladium chloride gave a mononuclear complex which was insoluble in common solvents. Reaction with $Ru(bpy)_2Cl_2$ gave the corresponding mononuclear complex (33).

However, the ^1H n.m.r. spectrum of this complex in acetonitrile was more complicated than expected and was found to change with time. This was suspected to be due to solvolysis of the complex with displacement of the bitetrazole

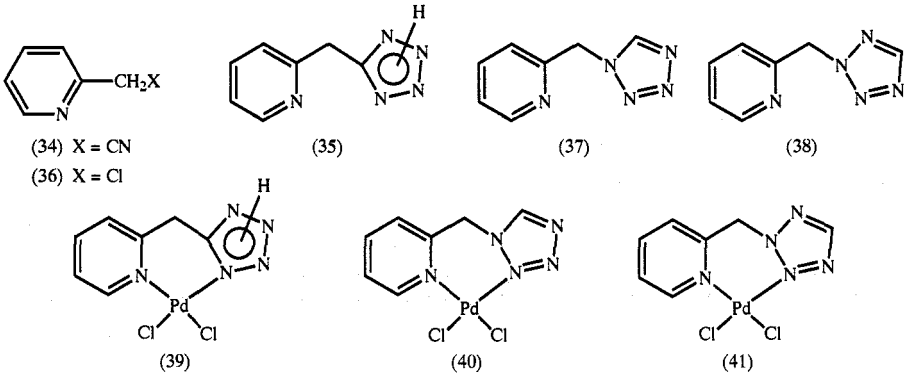
[40] Stolle, R., *Chem. Ber.*, 1922, **55**, 1289.
[41] Nelson, J. H., Takach, N. E., Henry, R. A., Moore, D. W., Tolles, W. M., and Gray, G. A., *Magn. Reson. Chem.*, 1986, **24**, 984.
[42] Ostrovskii, V. A., Koldobskii, G. I., Shirokova. N. P., and Poplavskii, V. S., *Khim. Geterotsikl. Soedin.*, 1981, 1563.

by acetonitrile and formation of $Ru(bpy)_2(MeCN)_2^{2+}$. This was confirmed by preparation of an authenic sample by a literature procedure[43] and comparison of its ^1H n.m.r. spectrum with that of the species produced from (33) in acetonitrile. Complete assignment of the spectrum (see Experimental section) of $Ru(bpy)_2(MeCN)_2^{2+}$ was achieved by a series of homonuclear decoupling experiments. Solvolyses of ruthenium(II) complexes containing π-excessive azole ligands is a known phenomenon (Steel *et al.* (1983)[6]). To avoid solvolysis of the complex the ^1H n.m.r. spectrum of (33) was recorded in the non-coordinating solvent CD_2Cl_2. As before, the spectrum contains only eight signals for the four pyridine rings of the bpy ligands due to the presence of a C_2 axis of symmetry in the complex. Again complete assignment of this spectrum was achieved by selective proton decoupling experiments. A notable feature of this spectrum is the high-field position of both the protons H6 of the bpy ligands (7·88 and 7·79 ppm). One of these protons is shielded by an adjacent pyridine ring while the other is shielded by an adjacent tetrazole ring. The fact that both protons are shifted to similar positions suggests that the tetrazole ring has a similar anisotropic ring current effect to that of pyridine. The π-excessive nature of the tetrazole groups is reflected in the electronic absorption spectrum of (33) which has a λ_{max} of 416 nm. This relatively high energy absorption of the MLCT transition is also consistent with the electrochemical data which show a relatively large difference (2·84 V) between the oxidation potential ($E^{\circ\prime} = +1{\cdot}43$ V) and the first reduction potential ($E^{\circ\prime} = -1{\cdot}41$ V). Compared to the related complex containing only one 2-t-butyltetrazol-5-yl group, viz. (20), this complex is considerably more difficult to oxidize but has a similar first reduction potential. Again this suggests that in the complex (33) there is a significant lowering of the metal-based HOMO by the π-excessive tetrazole rings with little effect on the bpy-based LUMO.

As described in the Introduction a number of ligands exist in which the two heterocyclic rings are separated by a methylene group. This prevents conjugation between the component heterocycles and introduces conformational flexibility to the ligand. It was therefore decided to prepare examples of such ligands containing tetrazole rings. Three isomeric pyridylmethyltetrazoles were prepared. Reaction of 2-pyridylacetonitrile (34) with sodium azide gave 5-(2-pyridylmethyl)tetrazole (35), which was purified by column chromatography. Reaction of 2-chloromethylpyridine (36) with tetrazole in the presence of sodium hydroxide gave a mixture of 1-(2-pyridylmethyl)tetrazole (37) and 2-(2-pyridylmethyl)tetrazole (38) in a 6:5 ratio but in low overall yield. These two isomers were separated with difficulty by column chromatography on silica gel. All three new ligands (35), (37) and (38) were characterized by ^1H n.m.r. and high-resolution mass spectrometry.

These three ligands readily formed palladium(II) complexes (39)–(41) by reaction with palladium chloride, and gave satisfactory elemental analyses. However, the ruthenium(II) complexes formed by reactions with $Ru(bpy)_2Cl_2$ all produced complex ^1H n.m.r. spectra, and failed to give satisfactory elemental analyses. These ligands appeared more reluctant to complex with ruthenium, presumably due to the lower stability of the six-membered chelate rings. The complexity of the n.m.r. spectra is probably also due to the fact that such six-membered

[43] Brown, G. M., Callahan, R. W., and Meyer, T. J., *Inorg. Chem.*, 1975, **14**, 1915.



(34) X = CN
(36) X = Cl
(35)
(37)
(38)
(39)
(40)
(41)

chelate rings can exist in two boat conformations.[44] Due to the difficulty in purifying these complexes no further studies were carried out.

In conclusion, eleven chelating tetrazole-containing ligands have been synthesized and their complexes with palladium(II) and ruthenium(II) prepared. ^{1}H n.m.r. spectroscopy, electronic absorption spectroscopy and cyclic voltammetry have been used to study the nature of the metal–ligand interactions in these complexes. It has been shown that the negatively charged tetrazolate group is a strong electron donor whereas protonated (or alkylated) tetrazoles produce a significant lowering in energy of the metal-based HOMO and raising in energy of the ligand-based LUMO of the ruthenium complexes. This allows pH control of the properties of the complexes. These ligands thus represent useful additions to the pool of chelating ligands that can be used to tune the physicochemical properties of transition metal complexes.

Experimental

General

Proton and carbon-13 n.m.r. spectra were recorded on a Varian XL-300 spectrometer. Spectra recorded in $CDCl_3$ were referenced relative to internal Me_4Si, and those recorded in $(CD_3)_2SO$ and CD_3CN were referenced against the solvent signals. Infrared spectra were recorded with a Perkin Elmer 1600 Fourier-transform infrared spectrophotometer as KBr disks. Ultraviolet–visible absorption spectra were recorded on a Perkin Elmer Lambda 2 spectrometer for acetonitrile or dichloromethane solutions.

The instrumentation, cells and electrodes and purification of solvent and electrolyte have been described recently.[45] Cyclic voltammetry measurements were made of solutions containing *c.* 1 mM complex in acetonitrile with 0·1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, by using a scan rate of 100 mV s^{-1} and a glassy carbon disk working electrode (area 0·07 cm^2). Ferrocene was used as an internal standard and potentials are given versus the saturated calomel electrode ($E^{\circ\prime}(Fc^+/Fc) = 0{\cdot}31$ V *v.* s.c.e.).

Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Mass spectra were recorded on a Kratos MS80RFA spectrometer. Elemental analyses were performed by the Chemistry Department, University of Otago, Dunedin. Solvents were purified according to standard literature procedures. Unless otherwise stated, reagents

[44] Minghetti, G., Cinellu, M. A., Bandini, A. L., Banditelli, G., Demartin, F., and Manassero, M., *J. Organomet. Chem.*, 1986, **315**, 387; Joshi, V. S., Sarkar, A., and Rajamohanan, P. R., *J. Organomet. Chem.*, 1991, **409**, 341.

[45] Downard, A. J., Hanton, L. R., McMorran, D. A., and Paul, R. L., *Inorg. Chem.*, 1993, **32**, 6028.

were obtained from commercial sources. $Ru(bpy)_2Cl_2$ [46] and $Ru(dmb)_2Cl_2$ [47] were prepared by literature procedures.

Preparation of Ligands

1-Methyl-5-(2-pyridyl)tetrazole (12) and 2-Methyl-5-(2-pyridyl)tetrazole (13)

To 5-(2-pyridyl)tetrazole (7) (2·0 g) in acetone (30 ml) were added methyl iodide (1·9 g) and aqueous sodium hydroxide (1·63 g in 3·5 ml of water). This mixture was stirred and heated under reflux for 3 h, diluted with water (30 ml), and extracted with chloroform. The extract was concentrated under vacuum to a yellow oil (1·66 g, 76%), shown by ^{1}H n.m.r. to be a mixture of the 1- and 2-methyl-5-(2-pyridyl)tetrazoles in a 3:7 ratio, respectively. The 2-methyl isomer slowly crystallized on standing (630 mg, 29%), and was separated from the remaining oil, washed with pentane, and recrystallized from ethyl acetate. The washings were combined with the oil, from which, upon standing, the 1-methyl isomer crystallized (436 mg, 18%); it was recrystallized from methanol. *1-Methyl-5-(2-pyridyl)tetrazole* (12), m.p. 91–92·5°C (Found (mass spectrum): $M^{+\bullet}$, 161·0703. $C_7H_7N_5$ requires $M^{+\bullet}$, 161·0701). ^{1}H n.m.r. ($CDCl_3$): 8·71, d, pyridyl H6′; 8·33, d, H3′; 7·89, t, H4′; 7·43, t, H5′; 4·49, s, Me. ^{13}C n.m.r. ($CDCl_3$): 149·3, C6′; 156·1, C4′; 125·2, C5′; 124·3, C3′; 36·9, Me. *2-Methyl-5-(2-pyridyl)tetrazole* (13), m.p. 105–106°C (Found (mass spectrum): $M^{+\bullet}$, 161·0700. $C_7H_7N_5$ requires $M^{+\bullet}$, 161·0701). ^{1}H n.m.r. ($CDCl_3$): 8·79, d, pyridyl H6′; 8·25, d, H3′; 7·88, t, H4′; 7·41, t, H5′; 4·43, s, Me. ^{1}H n.m.r. ($(CD_3)_2SO$): 8·85, d, H6′; 8·23, d, H3′; 8·11, t, H4′; 7·65, t, H5′; 4·55, s, Me. ^{13}C n.m.r. ($CDCl_3$): 150·3, C6′; 137·1, C4′; 124·8, C5′; 122·3, C3′; 39·7, Me.

Reaction of (7) (450 mg) in ethanol/water (1:1 v/v, 10 ml) containing sodium hydroxide (120 mg) and methyl iodide (650 mg) gave the two isomers in a 1:1 ratio in 48% yield (236 mg). Reaction of (7) (150 mg) in MeCN (5 ml) in the presence of potassium carbonate (150 mg) and methyl iodide (150 mg) gave the two isomers in a 2:3 ratio in 73% yield (120 mg).

2-t-Butyl-5-(2-pyridyl)tetrazole (15)

To t-butyl alcohol (25 ml) were added 5-(2-pyridyl)tetrazole (7) (500 mg), trifluoroacetic acid (3 ml) and concentrated sulfuric acid (3 ml). This mixture was stirred overnight at 25°C, then water (50 ml) added and the mixture made alkaline by the dropwise addition of sodium hydroxide (10 M). This solution was extracted with chloroform, and the extract concentrated under reduced pressure to give (15) as a pale yellow *solid* (375 mg, 54%), m.p. 75°C (Found (mass spectrum): $M^{+\bullet}$, 203·1171. $C_{10}H_{13}N_5$ requires $M^{+\bullet}$, 203·1171). ^{1}H n.m.r. ($CDCl_3$): 8·81, d, H6′; 8·28, d, H3′; 7·86, t, H4′; 7·39, t, H5′; 1·84, s, CMe_3. ^{1}H n.m.r. ($(CD_3)_2SO$): 8·84, d, H6′; 8·25, d, H3′; 8·11, t, H4′; 7·65, t, H5′; 1·86, s, CMe_3.

Reaction of (7) with t-butyl alcohol in the presence of dicyclohexylcarbodiimide and cuprous chloride according to a related literature procedure[34] gave a product, in 72% yield, that was shown by ^{1}H n.m.r. to be a 3:2 mixture of 1-t-butyl-5-(2-pyridyl)tetrazole (14) (characterized by a ^{1}H n.m.r. singlet at 1·78 ppm) and (15).

1-(2-Pyridyl)tetrazole (21)

To 2-aminopyridine (22) (200 mg) in acetic acid (5 ml) were added triethyl orthoformate (5 g) and sodium azide (300 mg). This solution was stirred and refluxed for 48 h. The solvent was removed under vacuum to afford (21) as a colourless *solid* (196 mg, 63%) (Found (mass spectrum): $M^{+\bullet}$, 147·0577; $[M-N_2]$, 119·0484. $C_6H_5N_5$ requires $M^{+\bullet}$, 147·0545; $[M-N_2]$, 119·0483). ^{1}H n.m.r. ($CDCl_3$): 9·57, s, tetrazole H5; 8·57, d, pyridyl H6′; 8·12, d, H3′; 8·01, t, H4′; 7·46, t, H5′.

5-(Pyrimidin-2-yl)tetrazole (24)

A mixture of pyrimidine-2-carbonitrile (25) (0·68 g) and sodium azide (0·49 g) was refluxed for 108 h in acetic acid (1·8 ml) and isopropyl alcohol (3 ml). The reaction vessel was then cooled to 4°C overnight, and the resulting precipitate was filtered off and dissolved in water

[46] Sullivan, B. P., Salmon, D. J., and Meyer, T. J., *Inorg. Chem.*, 1978, **17**, 3334.
[47] Mabrouk, P. A., and Wrighton, M. S., *Inorg. Chem.*, 1986, **25**, 526.

(40 ml). The solution was acidified with concentrated hydrochloric acid, and extracted with chloroform. The solvent was removed under reduced pressure to give (24) as a pale yellow *solid* (0·48 g, 50%), m.p. 225–228°C (Found (mass spectrum): $M^{+\bullet}$, 148·0499. $C_5H_4N_6$ requires $M^{+\bullet}$, 148·0497). ^1H n.m.r. ($(CD_3)_2SO$): 9·17, d, pyrimidinyl H4′, H6′; 7·82, t, H5′.

2,2′-Di(t-butyl)-5,5′-bitetrazole (33)

To t-butyl alcohol (70 ml) were added 5,5′-bitetrazole[41] (27) (900 mg), trifluoroacetic acid (6 ml) and concentrated sulfuric acid (5 ml). This mixture was stirred overnight at 25°C, then water added (100 ml), then sodium hydroxide was added until the solution was alkaline. The resulting solution was extracted with chloroform and the extract concentrated to give a solid *product* (1·06 g, 78%), m.p. 77°C (Found (mass spectrum): $M^{+\bullet}$, 251·1740. $C_{10}H_{18}N_8$ requires $M^{+\bullet}$, 251·1732). ^1H n.m.r. ($CDCl_3$): 1·85, s, CMe_3.

5-(2-Pyridylmethyl)tetrazole (35)

To 2-pyridylacetonitrile (34) (0·68 g) in acetic acid (1·8 ml) and isopropyl alcohol (3 ml) was added sodium azide (0·45 g). This mixture was refluxed at 150°C for 108 h. An additional quantity of solvent (4·5 ml isopropyl alcohol/2·7 ml acetic acid), and sodium azide (1 g) were added, and refluxing was continued for a further 24 h. The mixture was then diluted with water, and a small amount of concentrated hydrochloric acid added. The resulting solution was extracted with chloroform, and the extract concentrated under reduced pressure. The crude *product* was purified by column chromatography on silica gel. Elution with $CHCl_3$ gave (35) in 12% yield (Found (mass spectrum): $M^{+\bullet}$, 161·0702. $C_7H_7N_5$ requires $M^{+\bullet}$, 161·0701). ^1H n.m.r. ($CDCl_3$): 8·60, d, pyridyl H6′; 7·78, t, H4′; 7·44, d, H3′; 7·33, t, H5′; 4·58, s, CH_2.

1-(2-Pyridylmethyl)tetrazole (37) and 2-(2-Pyridylmethyl)tetrazole (38)

A mixture of tetrazole (100 mg), dimethylformamide (5 ml) and 2-chloromethylpyridine hydrochloride (257 mg) was heated and stirred at 100°C for 4 h. One pellet of sodium hydroxide was added, and stirring and heating were continued for a further 3 h; then the mixture was left stirring overnight. Water (5 ml) was then added, and the mixture extracted with chloroform. Concentration of the extract gave two isomers, which were separated by column chromatography on silica gel. Elution with $CDCl_3$ gave *2-(2-pyridylmethyl)tetrazole* (38) (Found (mass spectrum): $M^{+\bullet}$, 161·0705. $C_7H_7N_5$ requires $M^{+\bullet}$, 161·0701). ^1H n.m.r. ($CDCl_3$): 8·47, d, pyridyl H6′; 8·46, s, tetrazole H5; 7·61, t, H4′; 7·18, t, H5′; 7·09, d, H3′; 5·86, s, CH_2. Furthur elution gave *1-(2-pyridylmethyl)tetrazole* (37) (Found (mass spectrum): $M^{+\bullet}$, 161·0700. $C_7H_7N_5$ requires $M^{+\bullet}$, 161·0701). ^1H n.m.r. ($CDCl_3$): 8·88, s, tetrazole H5; 8·62, d, pyridyl H6′; 7·75, t, H4′; 7·34, m, H3′, H5′; 5·73, s, CH_2.

Preparation of Complexes

General Procedure for Preparation of Palladium Complexes

To a solution obtained by dissolving palladium(II) chloride (0·2–0·5 mmol) in hot 2 M HCl was added a methanolic solution of 1 equiv. of the ligand (0·2–0·5 mmol). Either immediate precipitation or slow crystallization of the palladium *complex* occurred.

(i) Reaction of (7) as above gave (8) as a yellow powder (62% yield) (Found: C, 25·3; H, 1·4; N, 24·2. $C_{12}H_8Cl_2N_{10}Pd_2$ requires C, 25·0; H, 1·4; N, 24·3%). ν_{max} (KBr) 3082, 2360, 1621, 1438, 668 cm^{-1}.

(ii) Reaction of (13) as above gave (16) as a yellow powder (77% yield) (Found: C, 24·9; H, 2·2; N, 20·5. $C_7H_7Cl_2N_5Pd$ requires C, 24·8; H, 2·1; N, 20·7%). ν_{max} (KBr) 3048, 1450, 754 cm^{-1}. ^1H n.m.r. ($(CD_3)_2SO$): 9·17, d, H6′; 8·49, t, H4′; 8·42, d, H3′; 8·01, t, H5′; 4·69, s, Me.

(iii) Reaction of (15) as above gave (17) as a yellow powder (78% yield) (Found: C, 31·8; H, 3·7; N, 18·3. $C_{10}H_{13}Cl_2N_5Pd$ requires C, 31·6; H, 3·4; N, 18·4%). ν_{max} (KBr) 2983, 1622, 1454, 1183, 749 cm^{-1}. ^1H n.m.r. ($(CD_3)_2SO$): 9·19, d, H6′; 8·48, t, H4′; 8·45, d, H3′; 8·01, t, H5′; 1·89, s, CMe_3.

(iv) Reaction of (24) as above, with gentle heating of the reaction mixture for 1 h, gave (26) as a yellow powder (67% yield) (Found: C, 21·4; H, 1·5; N, 28·1. $C_{10}H_6Cl_2N_{12}Pd_2 \cdot \frac{2}{3}MeOH$ requires C, 21·4; H, 1·5; N, 28·0%). ν_{max} (KBr) 3446, 3075, 2360, 1598, 1395, 1245 cm^{-1}.

(v) Reaction of (27) as above, with refluxing of the reaction mixture for 24 h, concentration of the solution to half the volume and cooling at 4°C, gave (29) as a yellow powder (60% yield) (Found: C, 7·5; H, 1·6; Cl, 10·9. $C_2HClN_8Pd.3H_2O$ requires C, 7·2; H, 2·1; Cl, 10·6%). ν_{max} (KBr) 3447, 1616, 1352, 668 cm^{-1}.

(vi) Reaction of (35) as above gave (39) as a yellow powder (76% yield) (Found: C, 26·4; H, 3·0; N, 18·3. $C_7H_7Cl_2N_5Pd.1·5MeOH.H_2O$ requires C, 26·8; H, 3·4; N, 18·4%). ν_{max} (KBr) 3505, 2921, 1609, 1478, 1104, 1023, 767 cm^{-1}.

(vii) Reaction of (37) as above gave (40) as a yellow powder (67% yield) (Found: C, 23·0; H, 2·5; N, 18·5. $C_7H_7Cl_2N_5Pd.2H_2O$ requires C, 22·5; H, 3·0; N, 18·7%). ν_{max} (KBr) 3528, 3076, 1607, 1091, 764 cm^{-1}.

(viii) Reaction of (38) as above gave (41) as a yellow powder (54% yield) (Found: C, 24·9; H, 2·3. $C_7H_7Cl_2N_5Pd$ requires C, 24·8; H, 2·1%). ν_{max} (KBr) 3473, 2924, 1635, 766 cm^{-1}.

General Procedure for Preparation of Ruthenium Complexes

A solution containing $Ru(bpy)_2Cl_2$ or $Ru(dmb)_2Cl_2$ (0·1–0·3 mmol) in water (5 ml) and ethanol (10 ml) was refluxed for 1 h. To this was added 1·1 equiv. of the ligand, and the mixture was stirred and refluxed for a further 4 h. The solvent was removed under reduced pressure to give a red-brown residue which was dissolved in water. Addition of an aqueous solution of ammonium hexafluorophosphate precipitated the product as a red or orange *solid*.

(i) Reaction of (7) with $Ru(bpy)_2Cl_2$, as described above, gave (9) as a mono(hexafluorophosphate) salt in 55% yield (Found: C, 43·0; H, 3·1; N, 17·1. $C_{26}H_{20}F_6N_9PRu.H_2O$ requires C, 43·2; H, 3·1; N, 17·5%). ^1H n.m.r. (CD_3CN): 8·538, 8·514, 8·488 (2H), 8·344, d, H3; 8·023, 8·047 (3H), 8·022, t, H4; 7·954, 7·921, 7·815, 7·691, 7·620, d, H6; 7·444 (2H), 7·425, 7·379, 7·306, t, H5. λ_{max} (ϵ) 466 nm (10400). $E°_{ox}$ +1·02 V; $E°_{red(1)}$ −1·50 V; $E°_{red(2)}$ −1·72 V. Addition of concentrated acid (HCl or HBF_4) gave λ_{max} (ϵ) 436 nm (10200), and $E°_{ox}$ +1·17 V.

(ii) Reaction of (7) with $Ru(dmb)_2Cl_2$, as described above, gave (10) as a mono(hexafluorophosphate) salt in 84% yield (Found: $[M-PF_6]^+$, 616·1519. $C_{30}H_{28}N_9{}^{102}Ru$, $[M-PF_6]^+$, requires 616·1511). ^1H n.m.r. (CD_3CN): 8·377, 8·352, 8·332 (2H), s, 8·318, d (pyt), H3; 7·990, t (pyt), H4; 7·748, 7·707, 7·665, 7·618 (pyt) 7·489, d, H6; 7·282 (pyt), 7·270, 7·252, 7·234, 7·213, t, H5; 2·580, 2·573, 2·563 (2Me), s, Me. λ_{max} (ϵ) 459 nm (9500). $E°_{ox}$ +0·91 V; $E°_{red(1)}$ −1·61 V; $E°_{red(2)}$ −1·84 V.

(iii) Reaction of (12) with $Ru(bpy)_2Cl_2$, as described above, gave (18) as a bis(hexafluorophosphate) salt in 89% yield (Found: C, 36·7; H, 3·1; N, 14·0. $C_{27}H_{23}F_{12}N_9P_2Ru.H_2O$ requires C, 36·7; H, 2·9; N, 14·3%). ^1H n.m.r. (CD_3CN): 8·63–8·47, m, 5H, H3; 8·25–8·08, m, 5H, H4; 7·96–7·81, m, 5H, H6; 7·63–7·43, m, 5H, H5; 4·59, s, Me. λ_{max} (ϵ) 423 nm (10400). $E°_{ox}$ +1·33 V; $E°_{red(1)}$ −1·37 V; $E°_{red(2)}$ −1·59 V; $E°_{red(3)}$ −1·82 V.

(iv) Reaction of (13) with $Ru(bpy)_2Cl_2$, as described above, gave (19) as a bis(hexafluorophosphate) salt in 64% yield (Found: C, 35·0; H, 3·0; N, 14·0. $C_{27}H_{23}F_{12}N_9P_2Ru.3H_2O$ requires C, 35·3; H, 3·2; N, 13·7%). ^1H n.m.r. (CD_3CN): 8·59 (2H), 8·53, 8·51, 8·43, d, H3; 8·17, 8·15 (3H), 8·09, t, H4; 8·02, 7·87, 7·84, 7·81, 7·75, d, H6; 7·54, 7·50 (2H), 7·48, 7·42, t, H5; 4·45, s, Me. λ_{max} (ϵ) 424 nm (9000). $E°_{ox}$ +1·31 V; $E°_{red(1)}$ −1·42 V; $E°_{red(2)}$ −1·61 V; $E°_{red(3)}$ −1·95 V.

(v) Reaction of (15) with $Ru(bpy)_2Cl_2$, as described above, gave (20) as a bis(hexafluorophosphate) salt in 76% yield (Found: C, 39·6; H, 3·4; N, 14·0. $C_{30}H_{29}F_{12}N_9P_2Ru$ requires C, 39·7; H, 3·2; N, 13·9%). ^1H n.m.r. (CD_3CN): 8·57 (2H), 8·52, 8·50, 8·43, d, H3; 8·18, 8·14 (3H), 8·09, t, H4; 7·92, 7·87, 7·82 (2H), 7·54, d, H6; 7·54, 7·51 (2H), 7·48, 7·42, t, H5; 1·75, s, CMe_3. λ_{max} (ϵ) 423 nm (12600). $E°_{ox}$ +1·29 V; $E°_{red(1)}$ −1·43 V; $E°_{red(2)}$ −1·65 V; $E°_{red(3)}$ −1·99 V.

(vi) Reaction of (27) with $Ru(dmb)_2Cl_2$, as described above, but without addition of the aqueous solution of ammonium hexafluorophosphate, gave (31) as a neutral complex (Found: MH^+, 607·1377. $C_{26}H_{24}N_{12}{}^{102}Ru$ requires MH^+, 607·1369). ^1H n.m.r. ($CDCl_3$): 8·03, 8·00, s, H3, H3′; 7·75, 7·64, d, H6, H6′; 7·07, 7·06, d, H5, H5′; 2·53 (2Me), 2·50 (2Me), s, Me.

(vii) Reaction of (32) with $Ru(bpy)_2Cl_2$, as described above, gave (33) as a bis(hexafluorophosphate) salt in 68% yield (Found: C, 38·8; H, 4·0; N, 15·8. $C_{30}H_{34}F_{12}N_{12}P_2Ru.2EtOH$ requires C, 39·0; H, 4·4; N, 16·1%). ^1H n.m.r. (CD_2Cl_2): 8·432, d, H3; 8·392, d, H3′;

8·158, t, H4; 8·056, t, H4′; 7·880, d, H6; 7·794, d, H6′; 7·645, t, H5; 7·447, t, H5′; 1·75, s, CMe_3. λ_{max} (ϵ) 416 nm (9000). E°_{ox} +1·43 V; $E^\circ_{red(1)}$ −1·43 V. In acetonitrile solution this complex was transformed to $Ru(bpy)_2(MeCN)_2^{2+}$, identical with a sample prepared by the literature procedure.[43] ^1H n.m.r. (CD_3CN): 9·37, d, H6; 8·56, d, H3; 8·42, d, H3′; 8·33, t, H4; 8·00, t, H4′; 7·91, t, H5; 7·64, d, H6′; 7·3, t, H5′; 2·32, s, Me.