Contribution from the Department of Chemistry,
University of Canterbury, Christchurch, New Zealand

Synthesis, Spectroscopy, and Electrochemistry of Ruthenium(II) Complexes of 6-(*N*-Pyrazolyl)- and 6-(*N*-Pyrazolylmethyl)-2,2′-bipyridines: New Tridentate Ligands

Alison J. Downard, Gene E. Honey, and Peter J. Steel*

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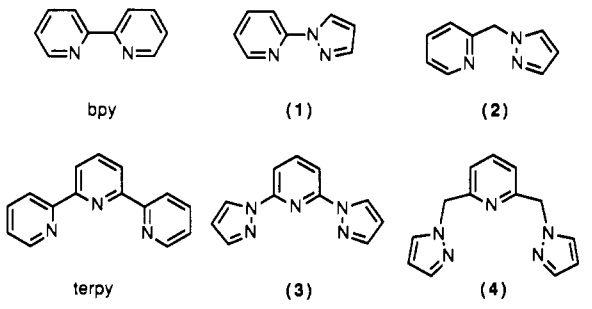
Four new tridentate ligands, **5a**, **5b**, **6a**, and **6b**, have been synthesized from 2,2′-bipyridine and their homoleptic bis(ligand) ruthenium(II) complexes, **12a**, **12b**, **13a**, and **13b**, prepared. Complete assignments of the ^{13}C and ^{1}H NMR spectra of the ligands and complexes have been made, and the origins of the coordination induced shifts are discussed. The electronic absorption spectra and redox properties of the complexes have been measured and are discussed in relation to previously reported complexes.

Introduction

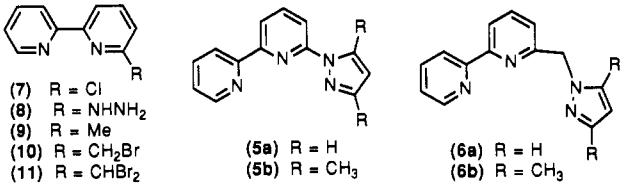
2,2′-Bipyridine (bpy) and 2,2′:6′,2″-terpyridine (terpy) are the most well-studied bidentate and tridentate chelating heterocyclic ligands.[1,2] In recent years there have been many studies of transition-metal complexes of biheteroaromatic ligands in which one or both of the pyridine rings of bpy are replaced by other nitrogen heterocycles.[3] Both π-deficient six-membered nitrogen heterocycles (azines) and π-excessive five-membered heterocycles (azoles) have been employed as ligand components, and the properties of the resulting complexes have been found to depend markedly on the specific heterocycles involved.[3] Thus, by the appropriate choice of ligand, it is now possible to tune, in a predictable manner, the ground- and excited-state properties[3,4] of complexes related to $Ru(bpy)_3^{2+}$. Pyrazole-containing ligands, such as the 2-(*N*-pyrazolyl)pyridines (**1**)[5] and the 2-(*N*-pyrazolylmethyl)pyridines (**2**),[6] have been the focus of much recent attention.



Planar tridentate terheteroaromatic analogues of terpy are less common.[7-9] Recently the syntheses and complexes of 2,6-bis(*N*-pyrazolyl)pyridine (**3**)[7] and 2,6-bis(*N*-pyrazolylmethyl)pyridine (**4**)[8] were described. Complexes of these ligands, which contain two π-excessive pyrazole rings, have very different properties to those of terpy complexes. For example the homoleptic bischelated ruthenium(II) complex of **3** has a very different visible absorption spectrum (λ_{max} = 377 nm) and first reduction potential ($E^{\circ\prime}$ = −1.66 V) from those of $Ru(terpy)_2^{2+}$ (λ_{max} = 475 nm; $E^{\circ\prime}$ = −1.27 V), indicating that the π*-LUMO of **3** is significantly higher in energy than that of terpy.[7] We now report the preparations and properties of related ligands and complexes in which only one of the three pyridine rings of terpy has been replaced by a pyrazole, viz. the 6-(*N*-pyrazolyl)-2,2′-bipyridines (**5**) and 6-(*N*-pyrazolylmethyl)-2,2′-bipyridines (**6**).

Results and Discussion

Ligand Syntheses. The 6-(*N*-pyrazolyl)-2,2′-bipyridines (**5**) were prepared from bpy by a four-step sequence, involving oxidation and chlorination, to give a 1:1 mixture[10] of 4-chloro–bpy and the required 6-chloro isomer **7**. These are readily separated by extraction with a nickel(II) solution that selectively removes the sterically less demanding 4-chloro isomer. We have found this procedure for the preparation of **7** to be more convenient than alternatives involving 2,2′-bipyridin-6-ones.[10,11] The chloride **7** was reacted with anhydrous hydrazine to give the corresponding hydrazinobipyridine **8**,[10] which underwent condensation with 1,1,3,3-tetramethoxypropane and with acetylacetone to give good yields of the desired 6-(*N*-pyrazolyl)-2,2′-bipyridines, **5a** and **5b**, respectively. Alternatively, direct reaction of **7** with the appropriate potassium pyrazolate in diglyme at 130 °C gave **5a** and **5b** in high yields.



The 6-(*N*-pyrazolylmethyl)-2,2′-bipyridines (**6**) were prepared in three steps from bpy by reaction with methyllithium and ox-

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Table I. NMR Chemical Shifts[a] and Coordination Induced Shifts (Given in Parentheses)[b]

	^{1}H NMR										
compd	H3	H4	H5	H3′	H4′	H5′	H6′	CH_2	R3″[c]	H4″	R5″[c]
5a	8.375	8.065	8.032	8.575	7.964	7.460	8.727		7.824	6.607	8.832
12a	8.689	8.536	8.385	8.550	7.976	7.224	7.337		7.151	6.605	8.827
	(+0.31)	(+0.47)	(+0.35)	(−0.03)	(+0.01)	(−0.24)	(−1.39)		(−0.67)	(0)	(−0.01)
5b	8.352	8.044	7.935	8.433	7.960	7.452	8.733		2.310	6.154	2.837
12b	8.641	8.444	8.383	8.521	7.957	7.249	7.275		1.396	6.186	2.977
	(+0.29)	(+0.40)	(+0.45)	(+0.09)	(0)	(−0.20)	(−1.46)		(−0.91)	(+0.03)	(+0.14)
6a	8.374	7.889	7.006	8.443	7.937	7.436	8.709	5.553	7.566	6.386	7.802
13a	8.669	8.419	8.123	8.447	7.941	7.255	7.826	5.677[d]	6.270	6.130	7.944
	(+0.30)	(+0.53)	(+1.12)	(0)	(0)	(−0.18)	(−0.88)	(+0.12)	(−1.30)	(−0.26)	(+0.14)
6b	8.361	7.885	7.031	8.419	7.940	7.438	8.709	5.389	2.195	5.942	2.354
13b	8.576	8.379	8.155	8.347	7.901	7.236	7.422	5.461	0.812	5.872	2.496
	(+0.22)	(+0.49)	(+1.12)	(−0.07)	(−0.04)	(−0.20)	(−1.28)	(+0.07)	(−1.38)	(−0.07)	(+0.14)

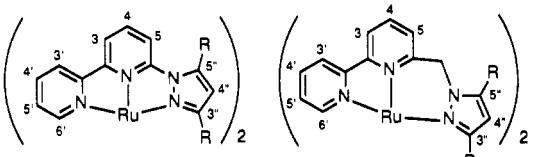
	^{13}C NMR[e]										
compd	C3	C4	C5	C3′	C4′	C5′	C6′	CH_2	R3″[c]	C4″	R5″[c]
5a	119.20	141.08	117.91	121.82	138.08	125.27	150.27		142.99	108.78	127.95
12a	121.63	139.11	112.94	125.61	138.77	128.24	153.75		147.02	111.23	133.65
	(+2.4)	(−2.0)	(−5.0)	(+3.8)	(+0.7)	(+3.0)	(+3.5)		(+4.0)	(+2.5)	(+5.7)
5b	118.39	140.63	116.23	121.86	138.20	125.14	150.30		13.72	110.04	15.44
12b	121.37	138.80	113.96	125.60	138.47	128.49	153.20		12.18	112.47	14.94
	(+3.0)	(−1.8)	(−2.3)	(+3.7)	(+0.3)	(+3.4)	(+2.9)		(−1.5)	(+2.4)	(−0.5)
6a	120.44	139.02	122.68	121.59	138.02	125.05	150.24	57.98	140.39	106.62	131.43
13a	124.51	139.48	128.24	125.15	138.17	127.67	153.85	55.53	144.21	108.34	137.02
	(+4.1)	(+0.5)	(+5.6)	(+3.6)	(+0.2)	(+2.6)	(+3.6)	(−2.5)	(+3.8)	(+1.7)	(+4.6)
6b	120.26	139.04	122.43	121.56	138.06	125.03	150.25	54.91	13.59	106.04	11.33
13b	124.43	139.55	127.59	124.78	138.31	127.67	153.81	52.26	12.44[f]	109.82	12.21[f]
	(+4.2)	(+0.5)	(+5.2)	(+3.2)	(+0.3)	(+2.6)	(+3.6)	(−2.7)	(−1.2)	(+3.8)	(+0.9)

[a] For deuterated acetonitrile solutions. [b] CIS = $\delta_{complex} - \delta_{ligand}$. [c] H or CH_3. [d] AB quartet, $\Delta\delta$ = 0.14 ppm. [e] Protonated carbons only. [f] Assignments may be interchanged.

idative workup[12] to give 6-methyl-2,2′-bipyridine (**9**), which was brominated[13] by using *N*-bromosuccinimide to give a 1:1 mixture of 6-bromomethyl-2,2′-bipyridine (**10**) and 6-dibromomethyl-2,2′-bipyridine (**11**). This mixture was not separated but was reacted with pyrazole and 3,5-dimethylpyrazole, under phase-transfer conditions,[14] to give in good yield the desired products **6a** and **6b**, respectively, along with unreacted **11**. The four new ligands were each purified by chromatography on silica and their structures confirmed by spectroscopic techniques.

The ^{1}H NMR spectra of the free ligands were all completely assigned from the characteristic coupling patterns of the individual protons and where necessary confirmed by decoupling experiments. The ^{13}C NMR spectra were then definitively assigned by means of ^{1}H–^{13}C heteronuclear two-dimensional correlation spectroscopy. Full assignments are given for the spectra of $CDCl_3$ solutions in the experimental section and for CD_3CN solutions in Table I. The chemical shifts for the free ligands are in accord with those expected by comparison with the spectra of the bidentate analogues **1**[5] and **2**.[6] Significant differences between the ^{1}H NMR spectra of **5** and **6** include the large upfield shifts of H5 and R5″ in the methylene-linked ligands **6** relative to the directly coupled ligands **5**; this mutual shielding of the protons indicates that in solution the conformation of **6** is such that the pyrazole and adjacent pyridine rings are approximately orthogonal with H5 lying over the plane of the pyrazole ring and R5″ lying over the plane of the pyridine ring.

Preparations of Ruthenium Complexes. Homoleptic bis-tridentate complexes of the ligands were prepared by reaction of the ligands with ruthenium trichloride in refluxing ethanol/water. The complexes were isolated as their hexafluorophosphate salts and characterized as $[Ru(L_2)](PF_6)_2$ by combustion analyses and NMR spectroscopy. Ligands **5a**, **5b**, and **6a** all gave reasonable yields of the expected complexes **12a**, **12b**, and **13a**, respectively. However, the ^{1}H NMR spectrum of the crude product obtained from reaction **6b** was considerably more complex than expected and indicated a mixture of products. Chromatography of this mixture on alumina allowed separation of the desired product **13b** and isolation of a small amount of a pure complex, which ^{1}H NMR spectroscopy showed to contain two nonequivalent ligands. This latter complex was identified as **14**, in which one of the ligands **6b** acts in a tridentate mode and the other is bidentate with coordination by the bipyridine component of **6b**.



(**12a**) R = H (**12b**) R = CH_3 (**13a**) R = H (**13b**) R = CH_3

The structure of **14** was deduced from the following features of the ^{1}H NMR spectrum: the presence of the coordinated chloride was indicated by a pyridine H6 proton at 10.301 ppm, a position characteristic[5d,15] of a proton (H6′b) deshielded by an adjacent chlorine; for each of the two methylene groups, the two protons were diastereotopic, one pair giving two doublets at 6.229 and 5.553 ppm and corresponding to a chelated tridentate ligand (CH_2a) and the other giving two doublets at 3.926 and 3.576 ppm and corresponding to two protons (CH_2b) strongly shielded by a pyridine ring. This shielding is only possible if the attached pyrazole ring is not coordinated to the metal. In accord with this, the signal for the adjacent proton (H5b) is shifted upfield to 6.029 ppm, consistent with approximately orthogonal pyridine and pyrazole rings of the bidentate ligand. The chemical shifts of the four methyl groups further confirm the structure as **14**. The complete ^{1}H NMR spectrum was assigned by two-dimensional homonuclear correlation spectroscopy, and all assignments and chemical shift values were in accord with structure **14**. These and the ^{13}C NMR chemical shifts are given in the Experimental Section. The lower yield for the formation of **13b** and the accompanying formation of **14** can be attributed to destabilization of **13b** due to a strong steric interaction between the *C5″*-methyl group of one ligand and the central pyridine ring of the other

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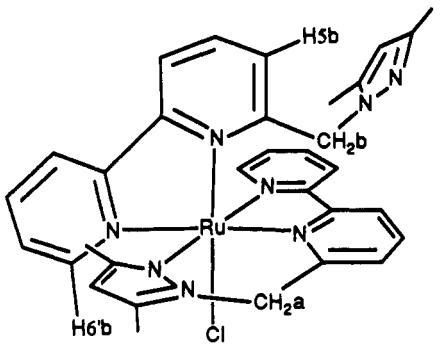
ligand. This interaction is much stronger with the six-membered chelate ring of **13b** than the five-membered chelate ring of **12b**. Nevertheless, the structure of **14** is novel in that within a single complex the same ligand coordinates in both a bidentate and a tridentate manner. Complexes in which terpy coordinates in a bidentate manner are known but are rare.[2,16]



(14)

NMR Spectra of the Ruthenium Complexes. The ^1H and ^{13}C NMR chemical shifts for the ruthenium complexes **12** and **13** are given in Table I, with the coordination-induced shifts (CIS = $\delta_{complex} - \delta_{ligand}$) in parentheses. Unambiguous assignments for all protons were made on the basis of spin–spin coupling information and selected decoupling experiments, and the carbon spectra were assigned by heteronuclear two-dimensional correlation spectroscopy. In complexes **12**, the two ligands are related by symmetry and so the complexes show the same number of signals as the corresponding free ligand. In complexes **13**, the pyrazole-containing chelate ring will exist in a boat conformation[5,17] that destroys the symmetry of the complex provided there is not rapid interconversion between different boat conformations. In the ^1H NMR spectrum of **13b**, the CH_2 protons give rise to a sharp singlet, indicating rapid interconversion of the boat conformers, whereas in **13a** the CH_2 protons give rise to an AB quartet, corresponding to two diastereotopic protons (axial and equatorial), which are not interconverting on the NMR time scale. The more rapid interconversion of conformers in **13b** can be attributed to steric interactions involving the methyl groups.

Some dramatic changes in ^1H NMR chemical shifts are observed on coordination to ruthenium, as revealed by the range of CIS values (+1.12 to −1.46 ppm) found in Table I. We[5d] and others[18] have identified a number of factors that contribute to the sign and magnitude of the observed CIS values. Ligand-to-metal σ donation, metal-to-ligand π back-donation, chelation-imposed conformational changes, coordinative disruption of interring conjugation and interligand through-space ring-current anisotropy effects have all been invoked to explain CIS values of tris(biheteroaromatic)ruthenium(II) complexes. These same factors seem to apply to the bis(triheteroaromatic)ruthenium(II) complexes **12** and **13**.

Large negative (upfield) CIS values are observed for the most laterally substituted protons in the ligands (viz. H6′ and R3″). These shifts are undoubtedly due to interligand through-space ring-current anisotropy effects since on complexation the protons involved all lie over the shielding plane of the central pyridine ring of the other coordinated ligand. The large positive (downfield) CIS values observed for H5 in the complexes **13** are due to conformational changes resulting from coordination. As discussed above, the free ligands **6a** and **6b** exist in conformations with approximately orthogonal pyrazole and pyridine rings, a situation that is not possible with tridentate coordination to ruthenium in the complex **13**. Conformational effects also undoubtedly contribute to the observed CIS values for protons adjacent to interring linkages. For example the C2–C2′ linkage of the free ligands **5** and **6** is likely to exist in a transoid conformation,[19] whereas the complexed ligand is constrained to a cisoid conformation. Accordingly the adjacent protons H3 and H3′ will experience different shielding effects in the free and complexed environments.

Protons such as H4, H4′, H4″ are not affected by the through-space anisotropy and conformational effects discussed above, and their CIS values should therefore reflect the other effects listed above to explain CIS values. Coordinative disruption of inter-ring conjugation has recently[5d] been proposed as a possible contributing factor to CIS values. It was suggested that there should be donation of π-electron density from a π-excessive heterocycle to a directly linked π-deficient heterocycle and that such conjugation would be disrupted by coordination to a metal. Such conjugation could exist in the ligands **5**, which contain a π-deficient pyridine ring directly linked to a π-excessive pyrazole ring, but not in the ligands **6** where the methylene bridge disrupts the conjugation. Since the CIS values at H4, H4′, and H4″ are similar in complexes **12** and **13**, it seems that this factor contributes little to the observed values.

The CIS values for these protons are also determined by interactions between the ligand and the metal. Ligand-to-metal σ donation will decrease the electron density at these sites and lead to positive CIS values whereas metal-to-ligand π back-donation will have the opposite effect and product negative CIS values. The CIS values for H4 have relatively large positive values, which suggests that ligand-to-metal σ donation is more important than metal-to-ligand π back-donation in the ground state of these complexes. In fact the values are similar to that (+0.46 ppm) previously[20] reported for $Ru(terpy)_2^{2+}$.

The ^{13}C NMR CIS values also cover a broad range (+5.7 to −5.0 ppm) but do not correlate in sign or magnitude with the ^1H values. This is principally because through-space ring-current anisotropy effects are considerably less important in ^{13}C NMR than in ^1H NMR. Thus C6′ and R3″ do not exhibit the large negative CIS values found for H6′ and R3″ protons. Conformational effects do seem to contribute to the ^{13}C NMR CIS values and probably explain the different CIS values for C5 in **12** and **13**. The observation that most of the CIS values are positive in sign further supports the suggestion that ligand-to-metal σ donation is more important than metal-to-ligand π back-donation.

Absorption Spectra and Redox Properties. Table II lists the electronic absorption maxima and redox potentials recorded in acetonitrile for complexes **12** and **13** and the corresponding values[7,21] for $Ru(terpy)_2^{2+}$ and $Ru(3)_2^{2+}$. In addition to strong (ϵ = 50 000 L cm^{-1} mol^{-1}) ligand-based $\pi \rightarrow \pi^*$ absorptions at

Table II. Absorption Maxima[a] and Redox Potentials[b]

complex	λ_{max}	$E^{\circ\prime}_{ox}$	$E^{\circ\prime}_{red(1)}$	$E^{\circ\prime}_{red(2)}$	$\Delta E_{ox-red(1)}$
12a	456	+1.16	−1.35	−1.58	2.51
12b	470	+1.06	−1.35	−1.59	2.41
13a	468	+0.96	−1.38	−1.63	2.34
13b	486	+0.89	−1.32	−1.61	2.21
$Ru(terpy)_2^{2+}$ [c]	475	+1.27	−1.27	−1.51	2.54
$Ru(3)_2^{2+}$ [d]	377	+1.25	−1.66[e]		2.91

[a] MLCT band in nm (±2 nm); measured in acetonitrile. [b] In volts vs SCE (±0.01 V); measured in 0.1 M $[Bu_4N][PF_6]/CH_3CN$. [c] Reference 21. [d] Reference 7. [e] Irreversible.

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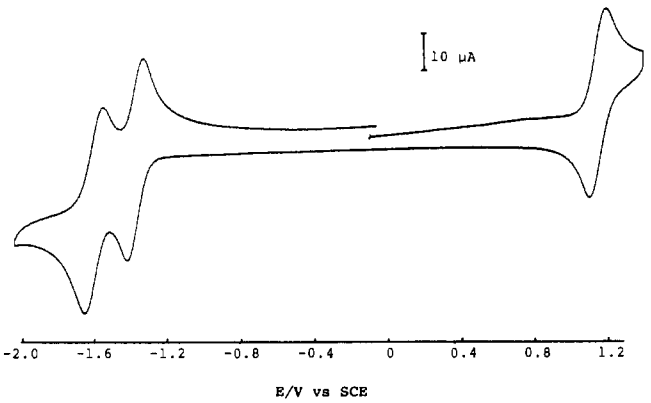

Figure 1. Cyclic voltammogram of complex **12a** (1 mM) in 0.1 M $[Bu_4N][PF_6]/CH_3CN$. Scan rate = 100 mV s^{-1}.

ca. 300 nm, the new complexes exhibit MLCT absorptions ($\epsilon \approx$ 9000 L cm^{-1} mol^{-1}) at an energy similar to that of $Ru(terpy)_2^{2+}$ and significantly different from that of $Ru(3)_2^{2+}$. Thus replacement of one of the three pyridine rings of terpy with a pyrazole ring does not have the profound effect on the MLCT absorption that two pyrazoles produce.

Further insight into the origin of these effects is provided by the electrochemical data. The complexes each exhibit a reversible one-electron oxidation and two reversible one-electron reductions, as shown in Figure 1 for complex **12a**. The significant differences between $Ru(terpy)_2^{2+}$ and $Ru(3)_2^{2+}$ were ascribed[7] to the higher energy of the π^* orbitals of **3** relative to terpy, as reflected in significantly different reduction potentials but similar oxidation potentials for the two complexes. However, this is not the case for the new complexes **12** and **13**, which have significantly different oxidation potentials from that of $Ru(terpy)_2^{2+}$. These differences can be attributed to structural features within the complexes. In the complex of **3** the π-excessive pyrazole ring is trans to another pyrazole, whereas in the complexes of **5** and **6** the pyrazole ring is trans to a π-deficient pyridine ring, thereby offering the possibility of synergic electron donation from the pyrazole through the metal to the pyridine. As a result, the properties of the complexes **12** and **13** are not intermediate between those of $Ru(terpy)_2^{2+}$ and $Ru(3)_2^{2+}$; **13b** for example absorbs at lower energy and has a lower ΔE_{ox-red} than $Ru(terpy)_2^{2+}$. As has been previously noted,[7] the introduction of electron-donating methyl groups also decreases the oxidation potentials by approximately 0.025 V per methyl group (e.g.: **12a** vs **12b**; ΔE = 0.10 V, for four methyl groups).

In summary, the new tridentate ligands **5** and **6** and their ruthenium complexes **12** and **13** have been prepared and their NMR, absorption spectra and redox properties studied. The complexes show significantly different properties from those of the corresponding complexes of terpy and **3**, thus demonstrating that ligands **5** and **6** offer new opportunities for tuning the ground- and excited-state properties of transition-metal complexes.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer. Chemical shifts are listed in ppm relative to tetramethylsilane and are considered accurate to 0.002 and 0.02 ppm for ^1H and ^{13}C shifts respectively. Homonuclear ^1H–^1H and heteronuclear ^1H–^{13}C correlation spectra were recorded in the usual manner.[22,23] Mass spectra were recorded by using a Kratos MS80RFA spectrometer. UV–visible absorption spectra were recorded by using a Perkin-Elmer Lambda2 spectrometer on acetonitrile solutions. Cyclic voltammograms were obtained with a PAR 173 potentiostat, a PAR 175 universal programmer and a Graphtec WX1200 recorder. A three-electrode cell was used, comprising a glassy-carbon working electrode (A = 0.07 cm^2), a Pt-wire auxillary electrode, and a Ag/Ag^+ (10^{-2} M in CH_3CN/0.1 M $[Bu_4N][PF_6]$) reference electrode. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} on solutions containing 1 mM complex and 0.1 M $[Bu_4N][PF_6]$ in CH_3CN. Ferrocene was used as an internal standard, allowing potentials to be reported vs SCE. Radial chromatography was performed on a Chromatotron (Harrison and Harrison) using Merck type 60 PF-254 with $CaSO_4 \cdot {}^1/_2H_2O$ silica gel. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected.

Preparation of 6-Chloro-2,2′-bipyridine (7). 2,2′-Bipyridine *N*-oxide (7.72 g) was chlorinated with phosphorus oxychloride according to a literature procedure[10] to give a mixture of 4-chloro-2,2′-bipyridine and 6-chloro-2,2′-bipyridine as a brown solid (6.01 g). To this mixture (6.0 g) in ethanol (20 mL) was added $NiCl_2 \cdot 6H_2O$ (1.3 g) in water (30 mL). The resulting solution was refluxed on a steam bath for 5 h. The solution was concentrated to dryness then redissolved in water (50 mL). Extraction with chloroform (3 × 50 mL) gave 6-chloro-2,2′-bipyridine (**7**) (3.16 g) as a solid. ^1H NMR ($CDCl_3$): 8.67, d, H6′; 8.41, d, H3′; 8.35, d, H3; 7.83, t, H4′; 7.80, t, H4; 7.35, d, H5; 7.34, m, H5′.

Treatment of the aqueous phase with an aqueous solution of potassium cyanide (1 g) followed by extraction with chloroform (3 × 50 mL) gave 4-chloro-2,2′-bipyridine (1.95 g). ^1H NMR ($CDCl_3$): 8.69, d, H6′; 8.57, d, H6; 8.46, d, H3; 8.40, d, H3′; 7.84, t, H4′; 7.36, m, H5′; 7.32, m, H5.

Preparation of 6-(*N*-Pyrazolyl)-2,2′-bipyridine (5a). (a) To 6-hydrazino-2,2′-bipyridine (**8**)[10] (120 mg) in ethanol (15 mL) were added 1,1,3,3-tetramethoxypropane (106 mg) and 2 drops of HCl, and the solution was stirred at reflux overnight. The product was concentrated to dryness and the residue dissolved in dilute HCl (1 M) and made neutral by addition of dilute sodium hydroxide. Extraction with chloroform followed by removal of solvent gave an oil (165 mg). Radial chromatography in petroleum ether/ethyl acetate gave 6-(*N*-pyrazolyl)-2,2′-bipyridine (**5a**) as a colorless solid (112 mg), mp 76–79 °C. Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.26; H, 4.54; N, 25.21. Found: C, 70.03; H, 4.47; N, 25.20. ^1H NMR ($CDCl_3$): 8.74, d, H5″; 8.70, d, H6′; 8.47, d, H3′; 8.33, d, H3; 8.02, d, H5; 7.96, t, H4; 7.86, t, H4′; 7.77, d, H3″; 7.35, m, H5′; 6.51, m, H4″. ^{13}C NMR ($CDCl_3$): 149.2, C6′; 142.0, C3″; 139.7, C4; 136.9, C4′; 127.0, C5″; 124.0, C5′; 121.1, C3′; 118.5, C3; 112.4, C5; 107.7, C4″.

(b) 6-Chloro-2,2′-bipyridine (**7**) was added to excess potassium pyrazolate (prepared from equimolar quantities of pyrazole and potassium metal at 70 °C in anhydrous diglyme), and the mixture was stirred at 120–130 °C for 3 days. The solvent was removed under reduced pressure to give a crude product mixture, which was purified as described above to give **5a** in 80% yield.

Preparation of 6-(*N*-3,5-Dimethylpyrazolyl)-2,2′-bipyridine (5b). (a) To **8** (130 mg) in ethanol (15 mL) was added acetylacetone, and the solution was stirred at reflux for 20 h. The product was concentrated to dryness to give a yellow solid (0.176 g). Chromatography on a silica gel column with chloroform as the eluting solvent gave 6-(*N*-3,5-dimethylpyrazolyl)-2,2′-bipyridine (**5b**), mp 74–75 °C. Anal. Calcd for $C_{15}H_{14}N_4$: C, 71.98; H, 5.64; N, 22.38. Found: C, 71.82; H, 5.73; N, 22.24. ^1H NMR ($CDCl_3$): 8.69, d, H6′; 8.35, d, H3′; 8.30, d, H3; 7.92, m, H4 & H5; 7.83, t, H4′; 7.33, m, H5′; 6.04, s, H4″; 2.80, s, 5″-CH_3; 2.33, s, 3″-CH_3. ^{13}C NMR ($CDCl_3$): 149.17, C6′; 139.28, C4; 136.90, C4′; 123.70, C5′; 121.06, C3′; 117.69, C3; 115.61, C5; 109.13, C4″; 15.14, 3″-CH_3; 13.66, 5″-CH_3.

(b) Reaction of **7** with excess potassium 3,5-dimethylpyrazolate in diglyme, according to the method described above, gave **5b** in 75% yield.

Bromination of 6-Methyl-2,2′-bipyridine. To 6-methyl-2,2′-bipyridine (**9**)[12] (740 mg) and *N*-bromosuccinimide (775 mg) in carbon tetrachloride (50 mL) was added dibenzoyl peroxide (50 mg), and the mixture was refluxed under nitrogen for 24 h. Filtration and removal of solvent gave a mixture of 6-bromomethyl-2,2′-bipyridine (**10**) (^1H NMR ($CDCl_3$): 8.68, d, H6′; 8.46, d, H3′; 8.33, d, H3; 7.83, m, H4 and H4′; 7.47, d, H5; 7.33, m, H5′; 4.64, s, 6-CH_2) and 6-dibromomethyl-2,2′-bipyridine (**11**) (^1H NMR ($CDCl_3$): 8.68, d, H6′; 8.46, d, H3′; 8.37, d, H3; 7.92, t, H4; 7.83, m, 2H, H4′ and H5; 7.33, m, H5′; 6.75, s, 6-CH) as an oil (0.90 g).

Preparation of 6-(*N*-Pyrazolylmethyl)-2,2′-bipyridine (6a). To a mixture of **10** and **11** (450 mg) were added pyrazole (160 mg), benzene (25 mL), 40% sodium hydroxide (5 mL), and a few drops of 40% tetrabutylammonium hydroxide. The resulting mixture was refluxed with vigorous stirring for 24 h. The organic phase was separated and the aqueous phase was then extracted with benzene. The solvent was removed from the combined benzene fractions to give an oil (246 mg). Radial chromatography using petroleum ether/ethyl acetate gave unreacted **11** as a solid and 6-(*N*-pyrazolyl)methyl-2,2′-bipyridine (**6a**) as an oil. Mass spectrum: M^+ calcd, 236.1062; found, 236.1064. ^1H NMR ($CDCl_3$): 8.68, d, H6′; 8.40, d, H3′; 8.30, d, H3; 7.82, t, H4′; 7.76, d, H4; 7.60, d, H5″ and H3″; 7.31, t, H5′; 6.98, d, H5; 6.34, t, H4″; 5.55, s, 6-CH_2. ^{13}C NMR ($CDCl_3$): 149.2, C6′; 139.9, C3″; 137.9, C4; 136.9, C4′; 130.0, C5″; 123.8, C5′; 121.4, C5; 121.2, C3′; 120.0, C3; 106.2, C4″; 57.6, 6-CH_2.

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Preparation of 6-((*N*-3,5-Dimethylpyrazolyl)methyl)-2,2'-bipyridine (6b). Reaction of a mixture of **10** and **11** (450 mg) with 3,5-dimethylpyrazole (224 mg) according to the above procedure gave 6-(*N*-3,5-dimethylpyrazolyl)methyl-2,2'-bipyridine (**6b**) as a colorless solid, mp 85-88 °C. Anal. Calcd for $C_{16}H_{16}N_4 \cdot {}^1/_2H_2O$: C, 70.31; H, 6.27; N, 20.49. Found: C, 69.69; H, 5.86; N, 20.00. ^{1}H NMR ($CDCl_3$): 8.68, d, H6'; 8.39, d, H3'; 8.27, d, H3; 7.82, t, H4'; 7.74, t, H4; 7.31, m, H5'; 6.82, d, H5; 5.90, s, H4''; 5.42, s, $-CH_2$; 2.27, s, 3''-CH_3; 2.25, s, 5''-CH_3. ^{13}C NMR ($CDCl_3$): 149.2, C6'; 138.0, C4; 136.9, C4'; 123.7, C5'; 121.2, C3'; 120.9, C5; 119.7, C3; 105.7, C4''; 54.5, $-CH_2$; 13.5 and 11.2, C3''- and C5''-CH_3.

Preparation of Ruthenium Complexes. General Procedure. To a solution of $RuCl_3 \cdot 3H_2O$ (1.0 mmol) in ethanol-water (90:10; 25 mL) was added the ligand (2.0 mmol), and the mixture was heated at reflux under a nitrogen atmosphere for 72 h. The solvent was then removed by rotary evaporation and the residue dissolved in water. The crude product was precipitated by dropwise addition of an ammonium hexafluorophosphate solution. Purification was by recrystallization from acetonitrile/diethyl ether or by column chromatography. ^{1}H and ^{13}C NMR spectra are given in Table I. Electronic spectra and redox potentials are listed in Table II.

(i) Reaction of **5a** as above gave bis[6-(*N*-pyrazolyl)-2,2'-bipyridine-*N*,*N'*,N2'']ruthenium(II) hexafluorophosphate (**12a**) as an orange-red solid in 55% yield. Anal. Calcd for $C_{26}H_{20}N_8RuP_2F_{12}$: C, 37.38; H, 2.41; N, 13.41. Found: C, 37.11; H, 2.17; N, 13.31.

(ii) Reaction of **5b** as above gave bis[6-(*N*-2,5-dimethylpyrazolyl)-2,2'-bipyridine-*N*,*N'*,*N2''*]ruthenium(II) hexafluorophosphate (**12b**) as a dark red solid in 50% yield. Anal. Calcd for $C_{30}H_{28}N_8RuP_2F_{12} \cdot CH_3CN$: C, 41.13; H, 3.34; N, 13.49. Found: C, 41.27; H, 3.06; N, 13.70.

(iii) Reaction of **6a** as above gave bis[6-(*N*-pyrazolyl)methyl-2,2'-bipyridine-*N*,*N'*,*N2''*]-ruthenium(II) hexafluorophosphate (**13a**) as a red solid in 67% yield. Anal. Calcd for $C_{28}H_{24}N_8RuP_2F_{12}$: C, 38.95; H, 2.80; N, 12.98. Found: C, 38.63; H, 2.95; N, 12.80.

(iv) Reaction of **6b** as above gave a red solid, which ^{1}H NMR showed to be a mixture of **13b** and **14**. Chromatography on alumina using chloroform/methanol as eluting solvents gave first bis[6-(*N*-3,5-dimethylpyrazolyl)methyl-2,2'-bipyridine-*N*,*N'*,*N2''*]ruthenium(II) hexafluorophosphate (**13b**), followed by chloro[6-(*N*-3,5-dimethylpyrazolyl)methyl-2,2'-bipyridine-*N*,*N'*,*N2''*][6-(*N*-3,5-dimethylpyrazolyl)methyl-2,2'-bipyridine-*N*,*N'*]ruthenium(II) hexafluorophosphate (**14**). ^{1}H NMR (CD_3CN) for the tridentate ligand: 8.51, d, H3; 8.33, d, H3'; 8.19, t, H4; 8.01, d, H5; 7.81, t, H4'; 7.30, d, H6'; 7.26, t, H5'; 5.79, s, H4''; 5.55, d, and 6.23, d, CH_2; 2.57, s, 5''-CH_3; 1.14, s, 3''-CH_3. ^{1}H NMR (CD_3CN) for the bidentate ligand: 10.30, d, H6'; 8.55, d, H3'; 8.29, t, H4'; 8.19, d, H3; 7.89, t, H5'; 7.62, t, H4; 6.03, d, H5; 6.00, s, H4''; 3.58, d, and 3.93, d, CH_2; 2.07, s, 3''-CH_3; 1.43, s, 5''-CH_3. ^{13}C NMR (CD_3CN): 155.5, 152.3, 138.1, 137.9, 137.8, 136.6, 127.4, 127.2, 125.4, 124.4, 124.1, 123.5, 122.5, 106.9, 104.0, 52.5, 52.3, 14.0, 13.4, 12.3, 10.3.

Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Evaluation of Electron-Transfer Sites in Ruthenium(II) Octaethylporphyrin Complexes of the Type (OEP)Ru(CO)(L)

K. M. Kadish,* P. Tagliatesta, Y. Hu, Y. J. Deng, X. H. Mu, and L. Y. Bao

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(OEP)Ru(CO) and (OEP)Ru(CO)(L) (where OEP = the dianion of octaethylporphyrin and L = an axial ligand) were electrochemically characterized in seven different nonaqueous solvents. The investigated complexes undergo two oxidations and either one or two reductions depending upon solvent. Both oxidations are ring centered, but this is not the case for reductions, which occur at either the porphyrin π-ring system or the central metal ion depending upon the specific solution conditions and the sixth axial ligand. An overall Ru(II) → Ru(I) reaction is suggested by thin-layer UV-visible spectroelectrochemical data in PhCN, CH_3CN or PrCN, while π-ring-centered reductions are suggested for the first reduction of (OEP)Ru(CO) in DMSO or py. Both reactions can be observed in THF with the initial reduction being ring centered followed by a conversion of the Ru(II) π anion radical to a Ru(I) form of the complex.

Introduction

The spectroscopic properties[1-4] and redox potentials[5-8] for oxidation and reduction of (OEP)Ru(CO)(L) (where OEP is the dianion of octaethylporphyrin and L is an axial ligand) have been extensively investigated over the last two decades. As a result of these studies, the formation of porphyrin π cation radicals and dications has been fairly well documented under a variety of experimental conditions. However, almost no data are available for singly reduced complexes of (OEP)Ru(CO)(L).

The one-electron reduction of (TPP)Ru(CO)(L) and ((*p*-X)-TPP)Ru(CO)(L) (where TPP = the dianion of tetraphenylporphyrin and L is a nitrogeneous base or solvent molecule) occurs at the porphyrin π-ring system and generates a Ru(II) porphyrin π anion radical,[9-12] which has been spectroscopically identified.[11] It was expected that (OEP)Ru(CO)(L) would also be reduced at the porphyrin macrocycle, but recent UV-visible data suggested that the electroreduction of (OEP)Ru(CO) in THF occurs at the metal center to give a Ru(I) porphyrin complex on the spectroelectrochemical time scale.[13] This reaction is investigated in the present paper, which characterizes (OEP)Ru(CO) redox reactions in seven different nonaqueous solvents. Each electroreduction and selected electrooxidations were investigated by thin-layer UV-visible and FTIR spectroelectrochemistry.

Experimental Section

Instrumentation and Procedure. Solution infrared spectra were measured by using an IBM 32 FTIR spectrometer and a light-transparent FTIR spectroelectrochemical cell whose construction has been described in the literature.[14] Thin-layer UV-visible spectroelectrochemical ex-

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