as photooxidants or photoreductants.

In summary, NMR and emission data indicate that the role of the insulating bridge in the 4,4′-position of the bipyridine dimer is to both spacially and electronically separate two similar metal centers from substantial communication with one another. It is clear that protons of conjugated ligands are affected by the presence of the metal centers and that the greatest effect is for protons on the coordinating component. The α protons neighboring the coordination site appear to shift downfield about 0.30 ppm for the heterocyclic ligand systems studied here. Further, similar metal centers attached to the *same* heterocyclic rings do interact electronically as noted by differences in their redox and electronic properties compared to the situation where only one metal center is attached. We are currently designing systems where two metal centers will be separated by an insulating spacer but where the metal centers will still be able to contact one another to facilitate electron transport. The bridging ligands currently being synthesized are bipyridine based but contain the bridge in the 6-position as opposed to the 4-position in Mebpy-Mebpy.

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Supplementary Material Available: A listing of decoupling parameters, results, and conclusions for NMR experiments with [(Mebpy-Mebpy)-$Re(CO)_3Cl$], [(bpp)$Re(CO)_3Cl$], and [(bpp)$(Re(CO)_3Cl)_2$] (4 pages). Ordering information is given on any current masthead page.

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Ruthenium(II) Complexes of N,N′-Bridged Derivatives of 2,2′-Biimidazole

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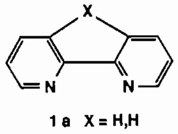
Ruthenium(II) complexes of the type $RuL_3[PF_6]_2$ and $RuL(bpy)_2[PF_6]_2$ have been prepared where L is an N,N′-bridged derivative of 2,2′-biimidazole. Molecular mechanics calculations have been employed to compare the geometries of these ligands to those of analogous 2,2′-bipyridine systems. Analysis of ^1H NMR spectra indicates that in the coordinated state the bridged biimidazoles show greater conformational mobility than their bipyridine counterparts. For the dimethylene-bridged biimidazole, the bite angle is too unfavorable to allow bidentate coordination and NMR evidence points to monodentate coordination in the mixed-ligand complex. The electronic spectra of the RuL_3^{2+} complexes show absorption at about 400 nm, which indicates a high-lying π^* state. This observation is reinforced by low oxidation potentials and high reduction potentials for these systems. The mixed-ligand complexes show an absorption band at even shorter wavelength, which we assign to the biimidazole MLCT state. The redox chemistry of these systems appears to be governed primarily by the bpy ligands.

Introduction

Ligands of the 1,2-diimine type have been widely employed in the complexation of a variety of transition-metal species, especially ruthenium(II).[1] The most commonly employed ligand of this type is 2,2′-bipyridine (bpy), which is readily able to adopt the planar conformation typically required for bidentate coordination. We have recently examined the effect of distorting bpy by the incorporation of a 3,3′-polymethylene bridge as depicted in structure **1**.[2] A series of ruthenium(II) complexes of the types RuL_3^{2+} and $Ru(bpy)_2L^{2+}$ were prepared and studied.[3] In general, it was found that although some flattening of the bridged bpy did occur upon complexation, ruthenium(II) could accommodate surprisingly distorted ligand geometries.



1a X = H,H
b X = CH_2
c X = $(CH_2)_2$
d X = $(CH_2)_3$
e X = $(CH_2)_4$

Other azabiaryl ligands such as 2,2′-bipyrimidine,[4,5] 2,2′-bipyrazine,[5,6] 1,10-phenanthroline,[7] 2,2′-biquinoline,[8,9] and 2,2′-bi[1,8]naphthyridine[9] have also been examined in hopes of tuning the properties of their metal complexes. These systems all share the common feature of chelating through an sp^2 nitrogen incorporated in a six-membered aromatic ring. In the absence of interfering substituents, the geometry of the resulting chelate ring is essentially invariant. If the coordinating nitrogen were instead incorporated into a five-membered heterocycle, however, the bite angle should be substantially diminished and the ligand's ability

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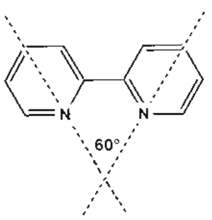
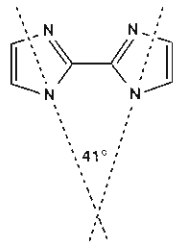
Table I. Calculated Geometries of Bridged Azabiaryl Ligands[a]

ligand	bridge (X)	dihedral angle[b] (α), deg	N–N′ dist,[c] Å	L–L′ dist,[d] Å
1a	H,H	0[e]	2.80	2.16
1b	$-CH_2-$	0	3.22	2.83
1c	$-(CH_2)_2-$	18	2.91	2.35
1d	$-(CH_2)_3-$	45	2.94	2.52
1e	$-(CH_2)_4-$	58	2.98	2.66
2a	H,H	0[e]	3.10	2.75
2c	$-(CH_2)_2-$	12	3.27	3.05
2d	$-(CH_2)_3-$	39[f]	3.23	3.05
		0	2.95	2.52
2e	$-(CH_2)_4-$	53	3.19	3.05
3	*o*-xylyl	60[f]	3.35	3.31
		0	2.84	2.34

[a] Calculated by using the programs PC MODEL and MMX available from Serena Software, Bloomington, IN. [b] For **1** this is defined as $N_1-C_2-C_{2'}-N_{1'}$ and for **2** and **3** as $N_3-C_2-C_{2'}-N_{3'}$. [c] Distance between coordinating nitrogens. [d] Distance between nitrogen lone-pair electrons. [e] Calculated for the planar cisoid conformation. [f] Planar and nonplanar energy minima were found for this system.

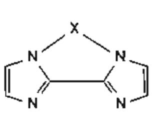
to chelate in a bidentate fashion should be influenced. As an extension of our earlier work on the effect of conformation on bpy coordination, we undertook a study of the coordinating properties of 2,2′-biimidazole (biim) with respect to both in-plane (bite angle) and out-of-plane distortions.



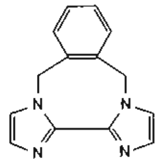


In comparing 2,2′-biimidazole with 2,2′-bipyridine, we will define the bite angle as being interior to the intersection of two lines, each of which passes through the chelating nitrogen and bisects the ring incorporating that nitrogen. Whereas the optimum bite angle for octahedral coordination is 90°, we find an angle of 60° for planar bpy and only 41° for planar biim.

The preparation of a series of *N,N′*-polymethylene-bridged derivatives of biim (**2c–e** and **3**) has recently been reported.(10) In light of the expected difference in bite angle, it became of interest to more carefully evaluate the conformational differences among **2**, **3**, and the analogous series of previously investigated 3,3′-bridged bpy derivatives **1b–e**.



2a X = H,H
b X = CH_2
c X = $(CH_2)_2$
d X = $(CH_2)_3$
e X = $(CH_2)_4$



3

Table I summarizes the results obtained from a simple molecular mechanics treatment of the systems in question. It is interesting to note that the dihedral angles ($N_1-C_2-C_{2'}-N_{1'}$) calculated for the bridged bipyridines **1b–e** are considerably less than earlier estimates[2] that were obtained by measurements from molecular models. Unlike the models, the computational approach takes into account π-overlap along the 2,2′-bond, which will tend to lessen the dihedral angle.

In comparing planar conformations of **2a** vs **1a**, one sees that the N–N′-distance of the former is greater by 0.30 Å. This increased distance makes the accommodation of short N,N′-bridges on biimidazole more difficult and longer bridges more favorable. The likelihood of preparing a monomethylene-bridged biimidazole appears to be remote while the tetramethylene-bridged system **2e** is less distorted from planarity than its bpy analogue **1e**. This situation leads to a lower conformational inversion barrier for **2e**, which can be conveniently measured by a variable-temperature NMR experiment and is found to be 10.6 kcal/mol.(10) The lone-pair distances (L–L′) for **1** are less than those for **2**. This, coupled with the arguments regarding bite angle, leads one to expect considerably more favorable coordination from bipyridines as opposed to biimidazoles.

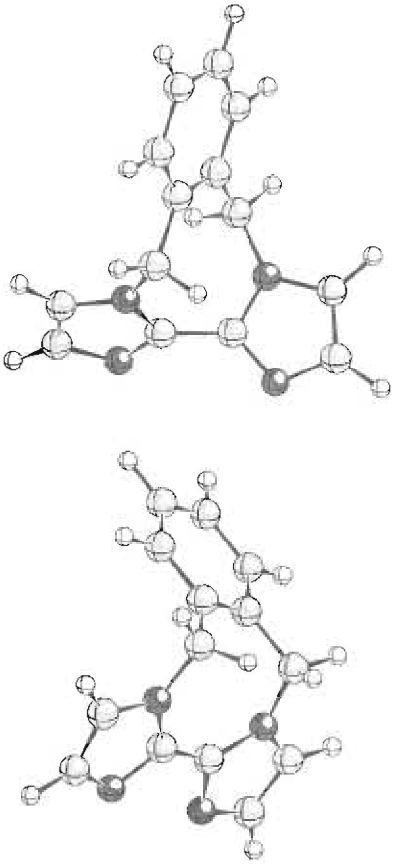


Figure 1. Ball and stick drawings of the planar (bottom) and twisted (top) conformations of 1,1′-(α,α'-*o*-xylyl)-2,2′-biimidazole (**3**).

It is noteworthy that two conformational energy minima were located for the trimethylene-bridged **2d** and the *o*-xylene-bridged **3**. From the computed total energies we predict that the planar conformations of both systems ($\alpha = 0°$) are slightly more stable. These planar conformations benefit from increased π-delocalization but suffer from an unfavorable nonbonded interaction between the two endo-$N-CH_2$ protons. From a symmetry standpoint, the planar conformation of either ligand possesses a mirror plane while the nonplanar conformation has a C_2 axis. Both forms of ligand **3** are illustrated in Figure 1.

Synthesis and Structural Properties

The preparation and properties of ligands **2** and **3** have been reported earlier.(10) The tris complexes of the type RuL_3^{2+} were prepared in the normal fashion by treating $RuCl_3$ with excess ligand in aqueous ethanol and precipitating the complex by the addition of NH_4PF_6. Purification was effected by chromatography on alumina with toluene/acetonitrile as eluent and crystallization of the complex from the concentrated eluent. The mixed-ligand complexes $Ru(bpy)_2L^{2+}$ were prepared in a similar manner using *cis*-$Ru(bpy)_2Cl_2$(11) in place of $RuCl_3$. Tris complexes of **2c** and **3** could not be prepared, while the tris(12) and mixed-ligand(13)

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Table II. ^{1}H NMR Chemcial Shift Data for Biimidazoles and Their Ruthenium(II) Complexes[a]

	biimidazole[b]				bipyridine[b]				
complex	H_4	H_5	bridge	$H_3/H_{3'}$	H_4/H_4'	H_5	$H_{5'}$	H_6	$H_{6'}$
2a	7.12	7.12							
2d	7.14	7.06	4.27/2.34						
2e	7.19	7.00	3.90/1.96						
Ru(**2a**)$_3^{2+}$	6.60	7.24							
Ru(**2d**)$_3^{2+}$	6.61	7.15	4.40/2.51						
Ru(**2e**)$_3^{2+}$	6.54	7.16	4.43/2.15						
Ru(**2a**)(bpy)$_2^{2+}$	6.40	7.25		8.43/8.42	8.00/7.96	7.44	7.32	7.93	7.82
Ru(**2d**)(bpy)$_2^{2+}$	6.39	7.19	4.43/2.55	8.43/8.41	8.03/7.98	7.48	7.31	8.03	7.81
Ru(**2e**)(bpy)$_2^{2+}$	6.35	7.17	4.46/2.13	8.44/8.42	8.03/7.95	7.47	7.31	7.94	7.79
Ru(bpy)$_3^{2+}$[c]				8.53	8.06		7.41		7.75

[a] Recorded at 300 MHz in CD_3CN and reported in ppm downfield from internal TMS. A complete listing of the NMR data for the ruthenium complexes is given in the supplementary material. [b] Proton-numbering scheme shown in Figure 2. [c] In accord with literature values.[1]

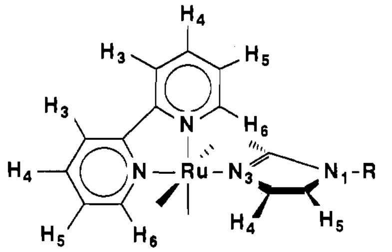

Figure 2. Ligand orientation and proton-numbering pattern for Ru(L)(bpy)$_2$[PF$_6$]$_2$ complexes (L = **2**, **3**).

complexes of **2a** have been previously reported.

The complexes were characterized by their 300-MHz ^{1}H NMR spectra, whose principal features are recorded in Table II. The proton-numbering scheme is indicated in Figure 2. High symmetry allows unambiguous assignment of the RuL$_3^{2+}$ complexes. For the free ligands **2** we assign the lower field imidazole resonance as H_4 due to the deshielding effect of the lone-pair electrons on N_3, which for N_1 are part of the π-system. Upon complexation, this signal shifts upfield to 6.54–6.61 ppm due to the shielding effect of the aromatic ring of an orthogonal ligand. This shielding effect is greater for the mixed-ligand complexes, where H_4 appears at 6.35–6.40 ppm (see Figure 2). In these complexes the orthogonal ligand is a bpy rather than a biimidazole. For both the tris and mixed-ligand complexes the biimidazole H_5 is shifted downfield due to charge depletion resulting from complexation (7.15–7.25 ppm) but is not much affected by the orthogonal ligand. Realizing that bpy induces a stronger shielding effect than biimidazole permits us to then distinguish between H_5, H_6 and $H_{5'}$, $H_{6'}$ on the bpy ligands of the mixed-ligand complexes. The resonances of H_5 and H_6 are less shielded and appear at lower field than $H_{5'}$ and $H_{6'}$. These assignments are also consistent with the corresponding chemical shift values for Ru(bpy)$_3^{2+}$. For the bpy ligands of the mixed-ligand complexes H_3, $H_{3'}$ and H_4, $H_{4'}$ cannot be differentiated.

The behavior of the bridge protons for the complexes of **2d**,**e** reveal an interesting feature of their Ru(II) complexes. As we have noted in earlier work, at room temperature both ligands **2d**,**e** are conformationally mobile with respect to rotation about the 2,2′-bond.[10] For the analogous bridged bpy derivatives **1d**,**e**, the former is conformationally mobile, while the latter is rigid on the NMR time scale. Upon tris complexation with Ru(II), both **1d**,**e** become rigid by NMR, while the biimidazole ligands **2d**,**e** remain conformationally mobile. This observation is consistent with our earlier discussion of calculated geometries, which predicts the existence of a planar minimum-energy conformation for **2d**. We also predict that tetramethylene bridging should be more readily accommodated in biimidazole than in bipyridine.

In a variable-temperature NMR experiment involving **2e**, we have observed that the broad signals for the α- and β-methylene protons split into two peaks at about −55 °C, allowing computation of an inversion barrier of 10.6 kcal/mol.[10] For the complex Ru(**2e**)$_3^{2+}$ we again observe only two signals for the methylene protons, but these remain essentially invariant down to −50 °C, indicating that the inversion barrier for **2e** is lower in the complexed state. This is most likely due to some flattening of the bound ligand. It is interesting that **1d** evidences the exactly opposite behavior, being conformationally mobile as the free ligand and rigid in the RuL$_3^{2+}$ complex.

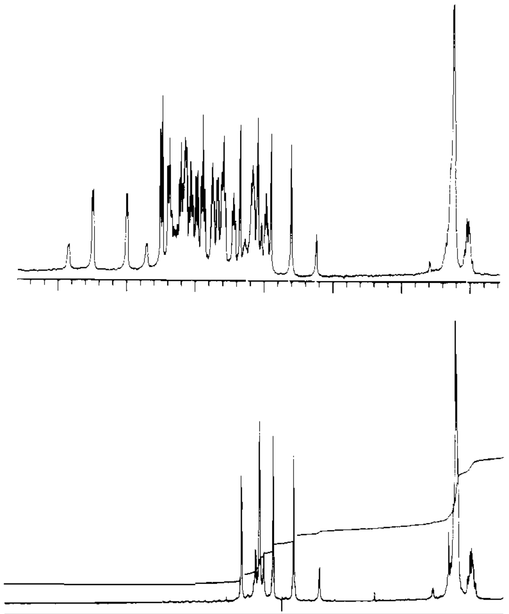

Figure 3. Downfield region of the ^{1}H NMR spectrum of Ru(**2c**)(bpy)$_2$(H$_2$O)[PF$_6$]$_2$ (top) and Ru(**2c**)(bpy-d_8)$_2$(H$_2$O)[PF$_6$]$_2$ (bottom) recorded in CD_3CN at 300 MHz.

Two of the systems under examination did not behave in a straightforward fashion and have been omitted from Table II. The first of these was the dimethylene-bridged system **2c**. As stated earlier, the tris complex of this species could not be prepared and the mixed-ligand complex appears to bind **2c** in a monodentate fashion. This behavior is best illustrated by the NMR spectra shown in Figure 3. The top spectrum shows the aromatic region for the complex which we expected to be Ru(bpy)$_2$(**2c**)$^{2+}$. Clearly, the spectrum is too complex for a detailed analysis although there does appear to be one set of protons having lesser intensities. Utilizing a recently developed reagent, Ru(bpy-d_8)$_2$Cl$_2$,[14] we prepared the complex at the bottom of Figure 3 in which all the bpy aromatic protons have disappeared. Now we clearly see a set of four equal-area singlets at 6.6–7.4 ppm as well as a lesser set of four peaks (one obscured by the peak at 7.1 ppm). The bridge methylene protons appear as two signals at 4.25 and 4.0

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Table III. Electronic Absorption Data for Ruthenium(II) Biimidazole Complexes (CH_3CN)

complex	λ_{max}, nm (ϵ)					
Ru(**2a**)$_3^{2+}$	396 (9650)		294 (23 300)	282 (29 350)	273 (26 400)	261 (24 100)
Ru(**2d**)$_3^{2+}$	402 (7600)	372 (6200, sh)	301 (22 200)	287 (26 500)	280 (23 800)	
Ru(**2e**)$_3^{2+}$	405 (7400)		306 (16 700)	293 (22 600)	285 (20 100)	
Ru(**2a**)(bpy)$_2^{2+}$	473 (8500)	432 (6800, sh)	329 (11 100)	289 (59 500)	253 (17 000)	242 (21 250)
Ru(**2c**)(bpy)$_2$(H_2O)$^{2+}$		450 (7900)		285 (69 900)	250 (17 700)	242 (20 250)
Ru(**2d**)(bpy)$_2^{2+}$	476 (10 150)	432 (6750, sh)	346 (11 200)	287 (56 800)	254 (18 800)	243 (21 000)
Ru(**2e**)(bpy)$_2^{2+}$	478 (10 900)	434 (7600, sh)	350 (11 600)	287 (61 800)	254 (19 700)	242 (21 800)
Ru(**3**)(bpy)$_2^{2+}$	476 (11 700)	432 (8700, sh)	354 (12 700)	285 (64 600)	257 (19 900)	245 (22 500)
Ru(bpy)$_3^{2+}$[a]	448 (12 500)	436 (11 400)		284 (71 000)		242 (18 700)

[a] In accord with literature values.[1]

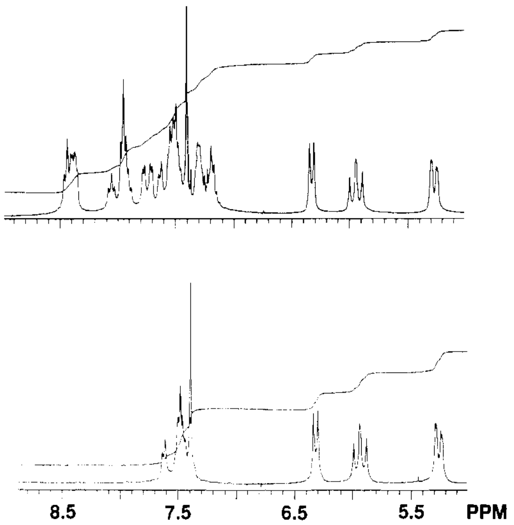

Figure 4. Downfield region of the ^1H NMR spectrum of Ru(**3**)(bpy)$_2$[PF_6]$_2$ (top) and Ru(**3**)(bpy-d_8)$_2$[PF_6]$_2$ (bottom) recorded in CD_3CN at 300 MHz.

ppm in the same approximate ratio as the aromatic signals. This spectrum indicates that **2c** is unsymmetrically bound to ruthenium, meaning that it must be monodentate. Careful purification did not change the ratio of the two sets of peaks, implying that they represent a pair of equilibrating conformers. When the complex is treated with excess bpy, the ligand **2c** is gradually displaced but the ratio of conformational isomers during the exchange process does not vary. Elemental analysis suggests that the sixth coordination site is occupied by a water molecule affording Ru(bpy)$_2$(**2c**)(H_2O)$^{2+}$.

The *o*-xylylene-bridged system **3** also shows unusual behavior. It will not form an RuL_3^{2+} complex although a mixed-ligand complex could be obtained in 41% yield. Figure 4 shows the aromatic region of the NMR spectrum of this material (top) as well as its bpy-d_8 analogue (bottom). The lower spectrum reveals the four Ar H protons from the bridging *o*-xylyl moiety at 7.65–7.4 ppm, a singlet at 7.4 ppm for H_5 and $H_{5'}$ of biimidazole, and two singlets at 6.30 and 6.34 ppm for H_4 and $H_{4'}$ of biimidazole. The benzylic methylene protons appear as two sets of overlapping doublets at 5.27 and 5.94 ppm. The appearance of the geminal benzylic protons as doublets indicates that they are magnetically nonequivalent and thus the ligand is conformationally rigid in the complex. As stated earlier, ligand **3** has two minimum-energy conformations, as shown in Figure 1. The conformation at the top of this figure would have C_2 symmetry, and its resulting mixed-ligand complex should exhibit the same symmetry, requiring the benzylic methylene protons to occupy only two magnetically nonequivalent environments, which would then show only two doublets in the NMR spectrum. The conformation at the bottom of Figure 1 has only a mirror plane, and thus its mixed-ligand complex would show C_s symmetry, as evidenced by the four observed benzylic doublets. This same argument would also account for nonequivalence of the biimidazole protons H_4 and $H_{4'}$, while H_5 and $H_{5'}$, being more remote from the source of asymmetry, do not resolve into two peaks.

Table IV. Half-Wave Potentials for Ruthenium(II) Biimidazole Complexes[a]

complex	$E_{1/2}$(oxidn)	$E_{1/2}$(redn)	
Ru(**2a**)$_3^{2+}$	+0.57 (135)		
Ru(**2d**)$_3^{2+}$	+0.54 (75)	−2.58[b,c]	
Ru(**2e**)$_3^{2+}$	+0.56 (100)	−2.24[b,c]	
Ru(**2a**)(bpy)$_2^{2+}$	+1.08 (80)	−1.66 (70)[d]	−1.96 (60)[d]
Ru(**2c**)(bpy)$_2$(H_2O)$^{2+}$	+1.19 (100)	−1.41 (100)	−1.58 (150)
Ru(**2d**)(bpy)$_2^{2+}$	+1.04 (80)	−1.44 (80)	−1.68 (100)
Ru(**2e**)(bpy)$_2^{2+}$	+1.06 (110)	−1.43 (90)	−1.66 (130)
Ru(**3**)(bpy)$_2^{2+}$	+1.13 (75)	−1.37 (85)	−1.61 (100)
Ru(bpy)$_3^{2+}$[e]	+1.30	−1.33	−1.52

[a] Potentials are in volts vs SCE for acetonitrile solutions, 0.1 M in TBAP, recorded at 25 ± 1 °C at a sweep rate of 200 mV/s. The difference between cathodic and anodic peak potentials (millivolts) is given in parentheses. [b] Same as for *a* except in dimethylformamide. [c] Irreversible, potential is given for the cathodic wave. [d] Reference 16; in DMF we observed a first reduction at −1.47 V (110) and a second reduction at −1.77 V (90). [e] In accord with literature values.[1]

Spectrochemical and Electrochemical Properties

Among the very extensive investigations centering on the properties of Ru(bpy)$_3^{2+}$ are several studies that describe the substitution of 2,2′-bipyrimidine or 2,2′-bipyrazine for one or more bpy ligands on the parent complex.[5a] The replacement of a pyridine CH by an sp^2 nitrogen increases the electronegativity of the aromatic ring system. In very general terms, the observed photochemical and electrochemical properties of the Ru(II) complexes of these ligands are consistent with the electronegativity sequence bipyrazine > bipyrimidine > bipyridine.[5,6] In fact, Ernst and Kaim have recently demonstrated that the properties of Ru(II) polyazines can be rationalized and predicted from knowledge of the ground-state basicities, π^*-orbital energies, and electron densities at the coordinating atoms.[15]

The ligand 2,2′-biimidazole differs markedly from the abovementioned series in that it consists of two six-electron, five-membered aromatic rings. The electron density of each ring will be higher, and hence its electronegativity will be concomitantly reduced. This fact has been previously noted by Dose and Wilson, who claim that the coordinated ligand **2a** is so easily deprotonated in acetonitrile that measurements had to be carried out in 125 μM $HClO_4$ to ensure that the complex was fully protonated.[13] Interestingly, our bridged biimidazoles obviate this problem by having no ionizable hydrogens.

Figure 5 depicts the electronic absorption spectra for the RuL_3^{2+} complexes of **2a,d,e**, and the data are collected in Table III. The spectra are all quite similar and show unusually short wavelength absorptions for what is presumed to be a metal-to-ligand charge-transfer (MLCT) transition. The diminished intensity for the less planar systems **2d,e** and their slight shift to longer wavelength are both consistent with our earlier observations with similar bridged bpy complexes.

Figure 6 displays the absorption spectra of the mixed-ligand complexes of **2c–e** and **3**. For the complexes involving bidentate

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Table V. Yield and Combustion Analysis Data for New Ruthenium Complexes

complex	yield, %	anal. calc, % C	H	N	anal. found, % C	H	N
$Ru(\mathbf{2d})_3[PF_6]_2$	15	35.45	3.28	18.38	35.51	3.33	18.31
$Ru(\mathbf{2e})_3[PF_6]_2$	29	37.66	3.77	17.57	37.47	3.70	17.30
$Ru(\mathbf{2c})(bpy)_2(H_2O)[PF_6]_2\cdot0.5$(toluene)	77	41.20	3.06	12.04	40.73	3.23	12.07
$Ru(\mathbf{2d})(bpy)_2[PF_6]_2\cdot0.5$(toluene)	44	42.21	3.25	12.12	41.89	3.21	11.99
$Ru(\mathbf{2e})(bpy)_2[PF_6]_2\cdot H_2O$	26	39.56	3.30	12.31	39.80	3.06	12.10
$Ru(\mathbf{3})(bpy)_2[PF_6]_2$	41	43.40	2.98	11.91	43.48	2.91	11.91

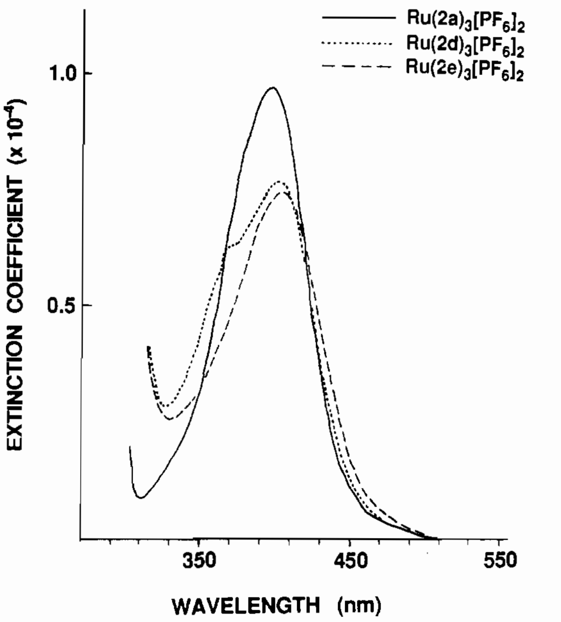

Figure 5. Electronic absorption spectra of ruthenium(II) tris(biimidazole) complexes, 10^{-4} M in CH_3CN.

biimidazoles (**2d**,**e** and **3**) the absorption has split into two bands, one at about 476–478 nm and another at 346–354 nm. The longer wavelength band resembles the peak and shoulder observed for $Ru(bpy)_3^{2+}$ and can be assigned to MLCT involving the bpy ligands. The shorter wavelength component is therefore due to MLCT involving the biimidazole ligand, but assignment to d–π_1* or d–π_2* is somewhat tenuous at this point. The absorptions below 350 nm for both sets of complexes agree well with π–π* ligand-centered transitions. It is noteworthy that the monodentate system, $Ru(\mathbf{2c})(bpy)_2(H_2O)^{2+}$, shows only the longer wavelength absorption lending credence to the hypothesis that the higher energy band for the other four mixed-ligand complexes involves charge transfer to biimidazole.

The electrochemical data for the complexes under consideration are given in Table IV. Most noteworthy are the RuL_3^{2+} complexes, which show a relatively facile, quasi-reversible oxidation in the range +0.54 to +0.57 V. These potentials can be compared with tris complexes of 2,2′-bipyrimidine (+1.69 V)[5a] and 2,2′-bipyrazine (+1.98 V),[5a] which are shifted to more positive potentials compared with $Ru(bpy)_3^{2+}$ due to the increased electronegativity of these ligands. The more electron-rich biimidazoles cause the opposite effect, raising the energy of the $\pi(t_{2g})$ orbitals by increased electron donation to the metal. The bridged biimidazoles **2c**–**e** may be considered as dialkylated derivatives of **2a** and show the expected inductive effect, resulting in a slight decrease of the oxidation potential. Thus the $E_{1/2}$(oxidn) values are greater for **2a** than for **2d** or **2e** in both the tris and mixed-ligand complexes. Similar behavior has previously been noted for imidazole vs *N*-methylimidazole.[17] The complex involving the monodentate **2c** behaves in a predictable fashion showing an oxidation potential of +1.19 V, intermediate between those of $Ru(\mathbf{2a})(bpy)_2^{2+}$ and $Ru(bpy)_3^{2+}$.

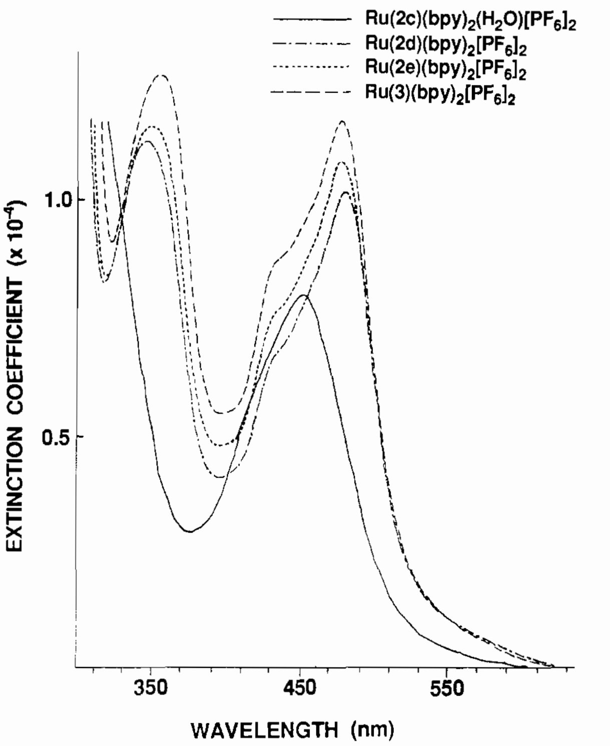

Figure 6. Electronic absorption spectra of ruthenium(II) bis(bipyridyl) biimidazole complexes, 10^{-4} M in CH_3CN.

It appears that the oxidation potentials depend, to a small extent, on the conformation of the biimidazole ligand. The more planar ligands are expected to interact more strongly with the metal t_{2g} orbital, raising its energy and lowering the oxidation potential of the complex. An increment of 20 mV is observed in going from the tetramethylene-bridged **2e** to the trimethylene-bridged system **2d** both in the tris and mixed-ligand complexes.

Within the solvent range of acetonitrile we are unable to observe any reductions for the tris complexes. Braun and co-workers have experienced similar results for the tris complex of 2-(2-pyridyl)imidazole.[18] In DMF we are able to observe an irreversible reduction wave at −2.58 V for $Ru(\mathbf{2d})_3^{2+}$ and at −2.24 V for $Ru(\mathbf{2e})_3^{2+}$. The first reduction of the mixed-ligand complexes is dominated by the π*-levels of the bpy ligands and hence shows only a modest decrease of 40–110 mV compared with that of $Ru(bpy)_3^{2+}$. Reduction of the mixed-ligand monodentate complex of **2c** is consistent with this effect and well in line with its higher homologues. All the complexes studied showed a good correlation between the $E_{ox} - E_{red}$ energy and the energy of the MLCT absorption band.[19]

Experimental Section

Nuclear magnetic resonance spectra were obtained in CD_3CN on a General Electric QE-300 spectrometer operating at 300 MHz, and chemical shifts are reported in parts per million downfield from Me_4Si.

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Ultraviolet spectra were obtained for CH_3CN solutions on a Perkin-Elmer 330 spectrophotometer.

Cyclic voltammograms were recorded with a BAS CV-27 voltammograph and a Houston Instruments Model 100 X-Y recorder. A three-electrode system was employed, consisting of a platinum-button working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The reference electrode was separated from the bulk of the solution by a cracked-glass bridge filled with 0.1 M TBAP in acetonitrile. Deaeration of all solutions was performed by passing high-purity nitrogen over the solution while measurements were made. Reagent grade acetonitrile was distilled twice from P_2O_5 under nitrogen. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP), was recrystallized from EtOAc/hexane, dried, and stored in a desiccator. Half-wave potentials were calculated as an average of the cathodic and anodic peak potentials.[20]

The preparation of the ligands has been previously reported.[10] *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ was prepared according to a procedure described by Meyer and co-workers,[11] and the deuterio analogue, *cis*-Ru(bpy-d_8)$_2Cl_2 \cdot 2H_2O$, was prepared as described earlier.[14]

Preparation of RuL_3^{2+} Complexes. A mixture of 1 equiv of ruthenium(III) chloride trihydrate (Aldrich) and 4.0 equiv of the appropriate ligand L in ethanol/H_2O (1:1) was refluxed under nitrogen for 15 h. The mixture was cooled and treated with 2.2 equiv of NH_4PF_6 dissolved in a minimum amount of H_2O. The resulting precipitate was collected, dried, and chromatographed on alumina, with CH_3CN or CH_3CN/toluene (3:2) as eluent. The complex crystallized from the eluent upon standing. Yields and elemental analyses are summarized in Table V.

Preparation of $Ru(bpy)_2L^{2+}$ Complexes. The same procedure was followed as outlined above for RuL_3^{2+}, using *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ or *cis*-Ru(bpy-d_8)$_2Cl_2 \cdot 2H_2O$ and the ligand L in a molar ratio of 1:1.1. Yields and combustion analyses are summarized in Table V.

Acknowledgment. We are grateful to the Robert A. Welch Foundation and the National Science Foundation (Grant CHE-8607935) for financial support of this work. The NMR spectrometer was partially funded by the NSF (Grant CHE-8616352). V.G. thanks Elf Aquitaine and the French Ministry of Foreign Affaires for a Bourse Lavoiser.

Supplementary Material Available: Table VI, giving ^1H NMR chemical shift assignments for ruthenium(II) complexes (1 page). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Novel (Cyclopentadienyl)nitroruthenium Complexes

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Ruthenium complexes of the type $[Ru(Cp)(L)_2(NO_2)]$ ($Cp = \eta^5\text{-}C_5H_5$; L = PPh_3 (triphenylphosphine), $^1/_2$ dppe (1,2-bis(diphenylphosphino)ethane), $^1/_2$ dppm (bis(diphenylphosphino)methane), $^1/_2$ dmpe (1,2-bis(dimethylphosphino)ethane)) were synthesized in three-step syntheses starting with $RuCl_3 \cdot 3H_2O$. The $[Ru(Cp)(L)_2(NO)](PF_6)_2$ complexes were then synthesized by reaction of $[Ru(Cp)(L)_2(NO_2)]$ with HPF_6. Characterization of these complexes was accomplished through UV-vis, ^1H NMR, and IR spectroscopies, cyclic voltammetry, and elemental analysis. The $[Ru(Cp)(dppe)(NO)](PF_6)_2$ complex displays two reversible one-electron electrochemical reductions in the absence of atmospheric oxygen.

Introduction

The coordination chemistry of (η^5-cyclopentadienyl)ruthenium complexes has been widely studied for the past 20 years.[1-3] While a large number of half-sandwich (cyclopentadienyl)ruthenium complexes have been reported, the majority of these complexes contain carbonyl ligands.[1-5] There has been a limited amount of research reported regarding (cyclopentadienyl)ruthenium complexes that do not contain carbonyl ligands, namely complexes of the type $[Ru(Cp)(L)_2(X)]^n$ (where $Cp = \eta^5\text{-}C_5H_5$, L = phosphine ligand, and X = anionic ligand (n = 0) or neutral ligand (n = 1+)).[6-11]

There are several examples of (cyclopentadienyl)nitrosylruthenium complexes.[9,12-15] Insertion of nitrosyl ligands into the coordination sphere of (pentamethylcyclopentadienyl)ruthenium has been under investigation by Bergman and co-workers, where they have reported the synthesis of a number of neutral complexes such as $[Ru(\eta^5\text{-}C_5Me_5)(NO)(PMe_3)]$ and $[Ru(\eta^5\text{-}C_5Me_5)(dmpe)(NO)]$.[12,13] In addition, the synthesis of the complex $[Ru(\eta^5\text{-}C_5H_5)(NO)(PMe_3)_2](PF_6)_2$ has been reported separately by Bruce and White[14] and Treichel.[9] Bruce and White attempted the synthesis of $[Ru(\eta^5\text{-}C_5H_5)(NO)(PPh_3)_2](PF_6)_2$ but found it to be unstable in the solid state.[14] With this paper we wish to report that this complex, as well as other (cyclopentadienyl)nitrosylruthenium complexes, is synthetically attainable and is stable in solution as well as in the solid state.

In addition to the synthesis and characterization of the $[Ru(Cp)(L)_2(NO)](PF_6)_2$ complexes, we also wish to report the synthesis and characterization of $[Ru(Cp)(L)_2(NO_2)]$ (L = PPh_3,

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