demonstrated that chelating thiolates can support an oligomeric array in which the metal atoms, although possessing essentially the same immediate coordination geometry, are rendered inequivalent by the chelate arrangement. This consideration should not be ignored in any interpretation of the spectroscopic inequivalence[30] of the metal centers of the metallothioneins and related proteins.

Acknowledgment. We thank S. Bristow for his considerable assistance and expertise in the recording and assignment of ^{13}C NMR spectra and the SERC for financial support (to J.R.N. and I.L.A.).

Registry No. $[PPh_4]_2[Cu_4(S_2\text{-}o\text{-}xyl)_3]$, 94957-36-5; [Cu(*N*-methylimidazole)$_4$][BF_4], 94957-37-6.

Supplementary Material Available: Listings of all the calculated atomic coordinates, anisotropic thermal parameters, isotropic thermal parameters for hydrogen atoms, remaining bond lengths and bond angles, and $|F_o|$ and $|F_c|$ values (40 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, and University of South Carolina, Columbia, South Carolina 29208

Study of a Cyclometalated Complex of Ruthenium by 400-MHz Two-Dimensional Proton NMR

P. REVECO,† J. H. MEDLEY,‡ A. R. GARBER,‡ N. S. BHACCA,† and J. SELBIN*†

Received July 25, 1984

Salts of the new cation $[Ru(bpy)_2(\mathbf{1})]^+$, where bpy = 2,2'-bipyridine and **1** = the cyclometalating ligand 2-(4-nitrophenyl)pyridine, have been prepared and characterized. A two-dimensional homonuclear decoupled autocorrelated Fourier transform ^1H NMR (HDCOSY) spectrum has allowed the assignment of all 23 of the distinguishable aromatic protons of the one benzene and five pyridine groups. This represents the first application of this new NMR technique to a metallic complex of this type.

Introduction

In recent years there has been an exponential increase in interest in the chemistry and physics of salts of tris(2,2'-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, and its substituted bipyridine and bipyridine-like derivatives.[1-3] Numerous complexes of the type $[Ru(bpy)_{3-x}L_x]^{n+}$, where x is 1 or 2 and L is some bidentate ligand that is not bipyridine-like, have also been prepared and studied spectroscopically,[1] but to our knowledge no such complexes have been prepared in which the ligand L is a cyclometalating species.

In the course of preparation of a series of new cyclometalated compounds of ruthenium, $[Ru(bpy)_{3-x}L_x]^{2-x}$ (bpy = 2,2'-bipyridine; L = 2-phenylpyridine; x = 1-3), which are being studied spectroscopically and electrochemically to evaluate their potential use as photocatalysts, it became apparent that the use of more sophisticated NMR techniques would be needed to properly interpret the spectra of these complexes. The first member of the new series to be prepared was $[Ru(bpy)_2(\mathbf{1})]PF_6$ (where **1** is 2-(4-nitrophenyl)pyridine). Its yield was low, but while alternative methods of preparation are being explored and other studies are in progress, we report here the use of two-dimensional Fourier transform ^1H NMR, which allows the ready interpretation of the three-dimensional structure of the complex and indeed the assignment of all 23 distinguishable aromatic protons! This represents, to our knowledge, the first application of such a technique to compounds of this type and complexity. We hope to be able to use this technique later in an NMR study of *photoexcited* molecules in this series.

Experimental Section

A. Compound Preparation. $[Ru(bpy)_2(\mathbf{1})]^+$ (bpy = 2,2'-bipyridine; **1** = 2-(4-nitrophenyl)pyridine) was prepared from the intermediate *cis*-$[Ru(bpy)_2(DME)]PF_6$ (DME = 1,2-dimethoxyethane), of which the preparation has already been described.[4] A freshly prepared solution of $[Ru(bpy)_2(DME)]PF_6$ in DME (10 mL, 5.0×10^{-2} M) was reacted with a DME solution of the ligand (40 mL, 200 mg, 100% excess) under argon. The solution was stirred and refluxed under argon for 30 min, and then an excess of triethylamine was added (to promote removal of the aromatic proton on the cyclometalating carbon). The mixture was refluxed for 24 h, the solvent distilled off, and the product chromatographed on an alumina column. The unreacted free ligand was eluted first with acetonitrile/toluene (1:1), and then the desired product came off. The dark red product was recrystallized from dichloromethane/ether, and the fine crystals were washed with ether and dried in vacuo. (Analytical analyses showed the compound to crystallize with 0.5 mol of water and 0.5 mol of methylene chloride, which is also the case for several other compounds in the series $[Ru(bpy)_2L]PF_6$, where L are other cyclometalating ligands such as azobenzene, substituted azobenzene, benzo[*h*]quinoline, and 2-phenylpyridine.)

B. NMR Experiments. The 2D COSY-45 and homodecoupled COSY (HDCOSY) spectra were acquired by using 2048 × 512 data matrices, resulting in 1024 × 1024 transforms after zero-filling in F1 and using the absolute value spectra. Both spectra were acquired with a 1024-Hz spectral window (SW).

The COSY-45 experiment uses a 45° mixing pulse to simplify the spectrum by limiting the cross peaks to directly connected transitions. The preparation and mixing pulses as well as the receiver reference phase were cycled for negative type peak selection. Matched Gaussian window functions were used in both domains.

The HDCOSY experiment[5] uses a 180° refocusing pulse between the preparation and mixing pulses to produce a spectrum in which the homonuclear coupling is collapsed in the F1 domain. There is a fixed delay between the preparation and mixing pulses set to half the normal acquisition time. The refocusing pulse follows an incremented delay. A 45° mixing pulse is necessary, and the 180° refocusing pulse must be carefully calibrated. All three pulses and the receiver reference phase are cycled so that only the coherence transfer echo is detected. A Gaussian window function was used in both domains.

All spectra were taken in $Me_2SO\text{-}d_6$ on a sample prepared by dissolving 20 mg of the compound in 0.5 mL of 100 atom % $Me_2SO\text{-}d_6$. Spectra were acquired at 400.133 MHz on a Bruker WH-400 spectrometer.

Results and Discussion

The low microsymmetry in the expected gross octahedral structure of $[Ru(bpy)_2(\mathbf{1})]^+$ (Figure 1) assures nonequivalence to all five pyridine groups. The molecule thus contains 23 nonequivalent aromatic protons, 20 on five monosubstituted pyridine rings and three on the trisubstituted benzene ring. Since the electronic environments of numerous pyridine hydrogen atoms would be very similar, their signals occur in a very narrow chemical shift range. Furthermore, their resonance patterns are made very

† Louisiana State University.
‡ University of South Carolina.

(1) Steel, P. J.; Lahousse, F.; Lerner, D.; Marzin, C. *Inorg. Chem.* **1983**, *22*, 1488 and the references contained therein.
(2) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617 and the references contained therein.
(3) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
(4) Connor, J. A.; Meyer, T. J.; Sullivan, B. P. *J. Am. Chem. Soc.* **1979**, *18*, 1388.
(5) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542.

0020-1669/85/1324-1096$01.50/0

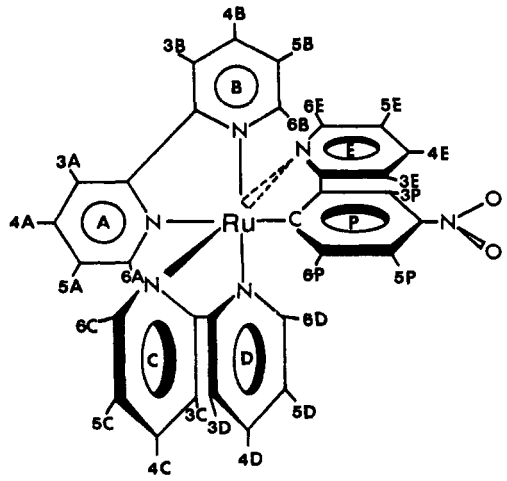

Figure 1. Gross octahedral structure of $[Ru(bpy)_2(1)]^+$, with the atoms identified for NMR purposes.

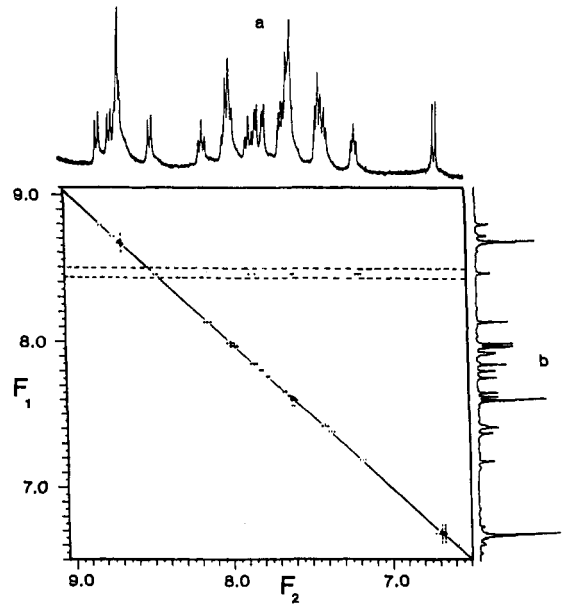

Figure 2. Contour plot of the HDCOSY spectrum of $[Ru(bpy)_2(1)]PF_6$.

complex by the spin–spin couplings of each pyridine proton to the other three protons present on the same ring. The resultant ^1H NMR spectrum of this molecule obtained at 400 MHz (Figure 2a) contains many overlapping complex multiplets, making its conventional ^1H NMR spectrum difficult to interpret. However, a two-dimensional (2D) NMR experiment that addes a new frequency axis allows one to separate their individual spectra.

In the conventional FT NMR experiment, a single short high-power radiofrequency (RF) excitation pulse induces a time-dependent RF signal in the sample due to the precessional frequencies of the observed nuclei. The signal, the free induction decay (FID), after Fourier transformation, yields the familiar intensity vs. frequency spectrum.

In the two-dimensional (2D) experiment a second time domain is used to produce a three-dimensional spectrum with the signal intensity as a function of two frequency domains. A generalized 2D experiment consists of a preparation pulse, an evolution period, a mixing pulse, and a detection period. The second time domain is generated by incrementing the evolution period. The two-dimensional spectrum is then the result of a modulation of the total spectrum as a function of the evolution period. The resulting data are stored as a two-dimensional array, with the normal FID's being stored in rows and the columns representing variation in the evolution period.

The resulting 2D spectrum consists of an F2 frequency domain (usually presented as the horizontal axis) that contains chemical shift information and an F1 domain (usually the vertical axis)

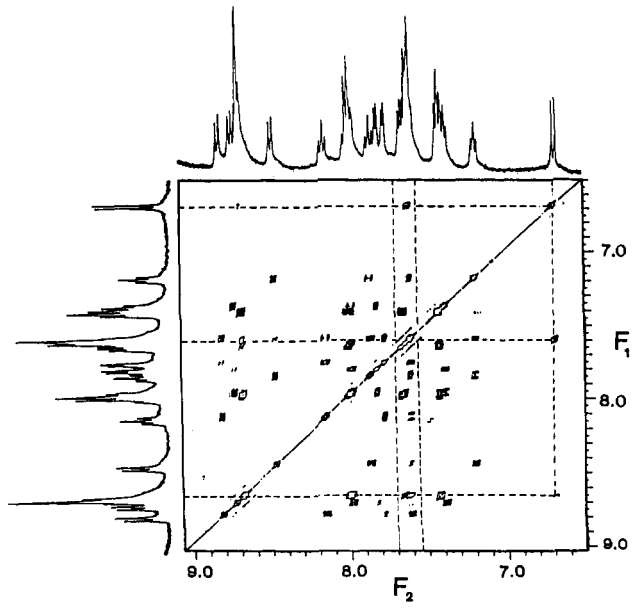

Figure 3. Contour plot of the COSY-45 spectrum of $[Ru(bpy)_2(1)]PF_6$.

that contains information concerning either spin–spin coupling between nuclei (as in the case of chemical shift correlation spectroscopy) or modulation due to the coupling constant itself (2D J resolved). These two domains are often presented as projections of signal intensity onto the vertical or horizontal axis.

The 2D technique in this study relies on magnetization transfer via spin–spin coupling to separate a spectrum with many overlapping multiplets into groups of signals that are coupled together (i.e., shared transitions). In the normal 2D shift correlation experiment (COSY for correlation spectroscopy), the two frequency domains are symmetrical so that the principle spectrum lies along a diagonal and peaks resulting from shared transitions are symmetrical across the diagonal.

In the COSY experiment, since both domains are symmetrical, the multiplets are spread out in two dimensions (Figure 3 shows the COSY spectrum of compound I). For a single signal it is easy to assign the signals that are coupled to it, through the projection perpendicularly onto the other axis (e.g., see the most upfield signal in the spectra of Figure 3). However, overlapping signals can be very ambiguous and difficult to assign, e.g. the multiplet near 7.6 ppm shown in Figure 3. The homonuclear decoupled COSY (HDCOSY) experiment, as proposed by Bax and Freeman,[5] uses a refocusing pulse to eliminate J modulation of the signal in the F1 domain. This produces a 2D spectrum in which the multiplicity appears only in the F2 domain (Figure 2a). The result of a projection in F1 is a broad-band-decoupled proton NMR spectrum (Figure 2b).

The HDCOSY spectrum (Figure 2) contains essentially the same information as the more common COSY experiment, but the interpretation is greatly simplified because the plot of a horizontal slice perpendicular to the F1 projection (as shown between dotted lines in Figure 2) yields a complete subspectrum containing not only the chemical shifts of shared transitions but also the complete coupling pattern of all protons that share transitions with the on-diagonal resonance (see Figure 4B). The interepretation of the subspectrum can be viewed as the interpretation of a simple small molecular weight compound.

In general, the first step in the interpretation of an HDCOSY spectrum is to plot the F1 projection and identify the chemical shifts of each unique proton. The next step is then to plot the horizontal rows perpendicular to the selected peaks. These rows are the individual subspectra and contain all resonances that are directly scalar coupled to the unique proton and show the correct coupling patterns. The multiplet at the unique chemical shift (the "on-diagonal" resonance) is the only proton that must be coupled to all other protons in the subspectrum. Assignment can often be made by matching the coupling constants in each off-diagonal

resonance with the coupling constant(s) in the on-diagonal resonance.

To simplify the interpretation of this compound, a table was prepared to reduce the complex total spectrum to groups of subspectra that have transitions in common. In this table (available as supplementary material), the unique chemical shifts are listed in rows and columns.

Careful study of this table allows it to be factored into six independent subgroups corresponding to the mutually exclusive subspectra of the individual aromatic rings in the compound. The resulting table is shown as Table I. (Artifacts show up as entries that are not reflected about the diagonal of the table). Assignment within the rings was then relatively simple. Figure 4 shows the individual subspectra for each ring arranged in groups.

For example, the horizontal projection corresponding to the peak at $\sigma = 8.79$ ppm yields the subspectrum plotted at the top of Figure 4A. This subspectrum contains the on-diagonal peak at $\sigma = 8.79$ ppm (indicated by X) as well as peaks at $\sigma = 8.13$, 7.75, and 7.58 ppm. The subspectra corresponding to these chemical shifts are also plotted in Figure 4A. An examination of each of these subspectra shows that they contain a peak at 8.79 ppm, confirming that each is in turn coupled to the peak at 8.79 ppm. Further, it can be noted that each spectrum contains a peak at 8.13, 7.75, and 7.58 ppm, confirming that all four peaks are mutually coupled. Additional peaks appear in some of the subspectra, in particular peaks at 8.67 and 6.67 ppm in the subspectrum corresponding to $\sigma = 8.13$ ppm (Figure 4A). An examination of the subspectra corresponding to these chemical shifts ($\sigma = 8.67$ ppm in Figure 4D and 6.67 ppm in Figure 4P) reveals these subspectra do not contain peaks at $\sigma = 8.13$ ppm; therefore, the peaks in the 8.13 ppm subspectrum are artifacts.

It is important to emphasize that the strength of the coupling is determined by the size of the coupling constant and not the intensity of the peak. In fact, it must be noted that for values of the evolution period, τ, equal to $2n\pi/J_{AX}$ the intensity of the cross peak is zero.[6]

The assignment of protons in each subgroup in Figure 4 is also relatively easy. The sharp doublet at 6.67 ppm (Figure 4P) was assigned to a proton on the substituted benzene since we expect broader signals from protons belonging to pyridyl groups due to coupling to the other three pyridyl protons and the quadrupole effects of the nitrogen. By examination of the coupling constants, we see that the proton at 6.67 ppm is coupled strongly to the multiplet at 7.593 ppm and weakly to the doublet at 8.66 ppm. We can therefore assign it to 6P position and assign the peak at 7.593 ppm to the 5P position and at 8.66 ppm to the 3P position. The remaining subspectra in the subgroup confirm this assignment.

Assigning the pyridyl group is only slightly more complicated. For example, subgroup A can be readily assigned, but we should not be misled by the relative intensities of the peaks in the subspectra. The doublet at 8.79 ppm can be assigned to the proton in position 3A, since we expect a downfield shift for position-3 protons due to the ring current of the ring in the same plane. On the other hand, the doublet at 7.75 ppm can be assigned to the proton in the 6A position. The coupling constants between protons 3A and 4A and protons 5A and 6A are too close to allow identification of which protons are which. However, independent decoupling experiments show that the upfield triplet corresponds to position 5A and the triplet downfield to position 4A. Observation of the second spectrum from the top in each subgroup (Figure 4) shows that the proton 3, which is certainly coupled to each proton 4, disappears (or nearly so) for the reason noted four paragraphs above (see ref 6).

Assignment for each other pyridyl group can be made by analogy. Subgroup C appears to lack an element, but simple inspection shows that the missing resonance occurs at 7.40 ppm. There is an overlap between the 5C and 5D protons that would not otherwise be apparent.

The assignment of all six aromatic rings is completely unambiguous; however, the absence of apparent coupling between rings

Table I. Scalar Couplings from the HDCOSY Data Matrix (Peak Intensities: W = weak, M = medium, S = strong)

	7.580	7.750	8.130	8.790	7.170	7.590	7.840	8.480	7.610	7.964	8.650	7.400	7.640	7.980	8.670	7.360	7.790	7.960	8.710	6.670	7.593	8.660
7.580	X	M	M	M	M			W			W									W		
7.750	S	X	M	M																		
8.130	S	S	X	W											W					W		
8.790	M	M	M	X																		
7.170	W				X	M	S	S														S
7.590					M	X	M	M												S		
7.840					S	S	X	VW														
8.480					S	M	W	X														
7.610									X	S	M	M								W		M
7.964									S	X	W	M	X	S								
8.650									M	W	X	M	S	X	W		W			W		
7.400									M	M	M	X	M	M	X					W		
7.640											M	M	X	S		X	M		S			W
7.980											M		S	X	W	M	X		M			
8.670	M										M	M	M	M	X	M	S	W	VW			
7.360										M						X	M		X			
7.790										S						M	S		M	VW		W
7.960													W			M	X					
8.710																M	M		X			
6.670					W		W													X	S	W
7.593								W							W			W		S	X	S
8.660								W					W		S		W	M		M	S	X

(6) Brown, L. R. *J. Magn. Reson.* **1984**, *57*, 513.

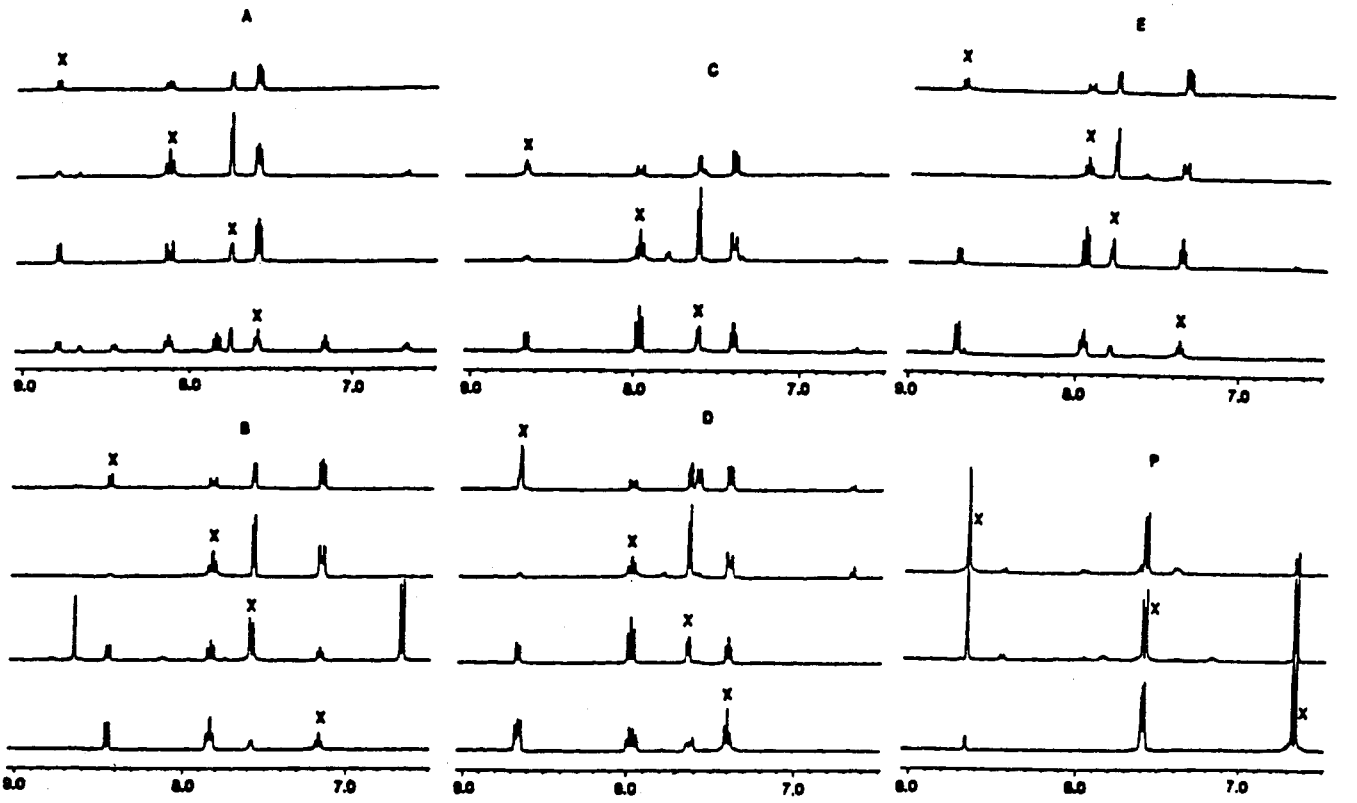

Figure 4. Subspectra from the HDCOSY spectrum arranged in subgroups of coupled peaks (X = on-diagonal element).

Table II. ^{1}H NMR Chemical Shifts (ppm) for $[Ru(bpy)_2(1)]^+$

proton	chem shift	proton	chem shift
3A	8.79	3D	8.67
4A	8.13	4D	7.98
5A	7.58	5D	7.40
6A	7.75	6D	7.64
3B	8.48	3E	8.71
4B	7.84	4E	7.96
5B	7.17	5E	7.36
6B	7.59	6E	7.79
3C	8.65	3P	8.66
4C	7.96	5P	7.59
5C	7.40	6P	6.67
6C	7.61		

makes the assignment to specific rings more difficult. In making the chemical shift assignments, according to the numbering system pictured in Figure 1, we expect an upfield shift for the protons in position 6. This shielding effect is due to the ring current of the pyridyl or phenyl group in the plane perpendicular to the plane of the ring where proton 6 lies (see Figure 1). Furthermore, since we expect the Ru–C bond distance to be slightly shorter than the Ru–N distance (as is the case in the entirely analogous octahedral d^6Rh(III) complex of 2-(4-bromophenyl)pyridine whose X-ray crystal structure has been determined[7]), we expect a greater upfield chemical shift for proton 6 on the phenyl group.

From geometrical considerations we can see (Figure 1) that if the Ru–C distance is shorter than the Ru–N distances, then proton 6B is closer to the neighboring ring current than the other protons 6, except for 6P.

With the likely shortened Ru–C bond we would also expect slightly lengthened Ru–N bond distances in both the nitrogen trans to the carbon (trans effect) and the one cis to the carbon that is a part of the same chelate ring as the carbon. There is good reason to expect these bond lengthenings from our[7] earlier structural study of an analogous cyclometalated rhodium(III) complex, $(Ru(1)_2Cl)_2$, wherein we found that the Rh–N is 0.05 Å *longer* than the calculated single-bond distance whereas the Rh–C (aryl) is 0.05 Å *shorter* than the calculated single-bond distance. Furthermore, we will make the assumption that the lengthening of the *trans*-Ru–N bond is greater than that of the cis-Ru–N bond. Of course, without more definitive information (as from an X-ray structure) this is by no means certain. However, if this assumption is not correct, then this would only interchange chemical shift assignments for some of the pyridyl groups. Therefore, with these assumptions and according to the numbering in Figure 1, the order of proximity of the protons in position 6 to the ring perpendicular to the plane of the ring where this proton lies is 6P, 6B, 6C, 6D, 6A, 6E. The assignments using this criterion and the subspectra in Figure 4 are finally all tabulated in Table II.

Acknowledgment. P.R. thanks the Universidad Tēcnica Federico Santa María, Valparaiso, Chile, for granting him study leave.

Registry No. $[Ru(bpy)_2(1)]PF_6$, 95156-39-1; *cis*-$[Ru(bpy)_2(DME)]PF_6$, 95156-41-5.

Supplementary Material Available: Table of scalar couplings from the HDCOS4 data matrix (1 page). Ordering information is given on any current masthead page.

(7) Fronczek, F. R.; Gutierrez, M. A.; Selbin, J. *Cryst. Struct. Commun.* **1982**, *11*, 1119.