

Chemistry of Bipyridyl-like Ligands. Isomeric Complexes of Ruthenium(II) with 2-(Phenylazo)pyridine¹

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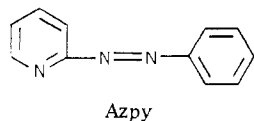
For further clarification of the nature of $d\pi-p\pi$ bonding in ruthenium(II) complexes the new bipyridyl-like ligand 2-(phenylazo)pyridine (Azpy) has been investigated. Three isomers of $[\text{Ru}(\text{Azpy})_2\text{Cl}_2]$ have been isolated and characterized. The least stable isomer (γ) isomerizes at 141 °C following first-order kinetics, $k = 7.9 \times 10^5 \text{ s}^{-1}$, $E_a = 34 \text{ kcal}$, and $\Delta S^\ddagger = 1 \text{ eu}$. A simple edge-twisting mechanism is suggested. IR, ¹³C NMR, cyclic voltammetry, and visible spectral data have been employed to characterize the complexes. It is concluded that the α isomer is cis (C_2), the β isomer is cis (C_1), and the γ isomer is trans (C_{2h}). Azpy is shown to behave as a strongly π -accepting ligand stabilizing ruthenium(II).

Introduction

In recent years much study has been devoted to ruthenium(II) complexes of 2,2'-bipyridyl (bpy). This is due, in part, to a number of factors. Ruthenium(II) is well recognized as a metal ion capable of entering into $d\pi-p\pi$ back-bonding with π -acceptor ligands;² bpy is such a ligand. π back-bonding, in addition to the conventional σ bonding, gives rise to a number of interesting properties. Charge-transfer luminescence of ruthenium(II)-polypyridyl complexes is one such property which has been well studied.³ But perhaps the most important recent utilization of the charge-transfer excited state of $\text{Ru}^{\text{II}}\text{bpy}$ is as a catalyst for the photolysis of water.^{4,5}

A number of recent papers have reported on a variety of chemical reactions of $[\text{Ru}(\text{bpy})_2\text{X}_2]$ complexes,⁶ much of the novelty of these reactions can be ascribed to the π interactions between metal ion and ligand. In spite of this activity, few papers have reported on ruthenium(II) with new π -acceptor ligands. This is probably due to the relative ease of synthesis of ruthenium-polypyridyl complexes and not to a lack of such behavior in similar systems.

It appears to us that there are a wide variety of potential ligands capable of acting as both σ donors and π acceptors; these should be capable of forming ruthenium(II) complexes which will have chemical properties somewhat different from those of bpy depending largely on the extent of π back-bonding. One ligand of this type is 2-(phenylazo)pyridine (Azpy). The ligand properties of Azpy have hardly been



investigated, there being reports only on iron(II),⁷ iron(II) and nickel(II),⁸ and mercury(II)⁹ complexes. Since the azo linkage in this ligand is involved in a π system and is a potential π

acceptor, we have undertaken a study of this ligand with ruthenium(II). One set of isomeric complexes of Azpy is described in this paper.

Experimental Section

Materials. Reagents were used as received. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Mathew-Bishop Co., Malvern, PA; organics were from Aldrich Chemical. 2-(Phenylazo)pyridine was prepared by a modification of the method reported by Campbell et al.¹⁰ Thin-layer chromatography (TLC) plates were precoated TLC sheets, Silica Gel 60F-254, from EM Laboratories, Inc., Elmsford, NY. Tetrabutylammonium perchlorate was prepared from the bromide and sodium perchlorate in water and recrystallized from acetonitrile-water. $[\text{Ru}(\text{Me}_2\text{SO})_4\text{Cl}_2]$ was prepared as described by Evans et al.¹¹

Methods. Infrared spectra were obtained on a Perkin-Elmer 283, using mineral oil and halocarbon mulls smeared on polished CsI plates. Mulls were prepared by grinding in a dental amalgamator ("Wig-L-Bug"). UV-visible spectra were recorded by using a Cary 17-D with matched silica cells. ¹³C NMR spectra were obtained on a Bruker 90-MHz instrument. Photoacoustic spectra were kindly provided by Dr. Fred Walters; data were obtained on samples ground with alumina (ca. 1:50).

Cyclic voltammetry data were obtained with a PAR electrochemical unit, Model 170, on dichloromethane solutions ca. $2 \times 10^{-3} \text{ M}$ in complex (0.1 M in tetrabutylammonium perchlorate supporting electrolyte). Solutions were outgassed with nitrogen; an ordinary SCE reference electrode was dipped directly into the solution. Platinum wire working electrodes and counterelectrodes were used. Multiple sweeps at 100 mV/s showed no indications of irreversibility.

For TLC, chloroform solutions were spotted on plates and developed first with diethyl ether and then with absolute ethanol. R_f values (isomer, color, ether, ether followed by ethanol): α , blue, 0.06, 0.55; β , purple, 0.02, 0.37; γ , green, 0.22, 0.47.

Kinetics were run by placing a *m*-dichlorobenzene solution (10^{-4} M) of the γ isomer in a flask in an oil bath (temperature controlled $\pm 0.1 \text{ }^\circ\text{C}$). Samples were removed periodically and cooled to room temperature, and the absorbance was measured at 430 nm. At this wavelength (which is a minimum in the α and β spectra) the α , β , and γ isomers have absorbance values of 1150, 1830, and 8280 $\text{L mol}^{-1} \text{ cm}^{-1}$, respectively. Contribution from the β isomer was assumed negligible (TLC data) and the concentration of the α isomer was calculated. Because of our performing a minimum number of experiments, the data should be considered as preliminary. However, at all three temperatures good linear first-order plots were obtained.

Analyses were performed by Baron Consulting Co., Orange, CT 06477.

Preparations. 2-(Phenylazo)pyridine, $\text{C}_{11}\text{H}_9\text{N}_3$ (Azpy). A 10.8-g sample of 2-aminopyridine is added to a solution of 54 g of NaOH in 54 mL of water containing 7 mL of benzene. Over a 10-min period, 12.4 g of nitrosobenzene is added while the mixture is shaken and warmed on the steam bath. After an additional 10-min heating, the mixture is extracted three times with 200-mL portions of benzene

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and the benzene solution is treated with decolorizing charcoal and then evaporated to an oil, which is finally dried in vacuo. The oil is then dissolved in hot petroleum ether (850 mL), and the mixture is decanted from a dark brown residue and cooled in dry ice to crystallize.

The petroleum ether recrystallization is repeated if necessary: yield 12.7 g; mp 32–34 °C.

β -Dichlorobis[2-(phenylazo)pyridine]ruthenium(II). A crude mixture of the isomers is prepared by mixing 2.00 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 2.80 g of Azpy in 100 mL of absolute ethanol and refluxing for 2 h. After cooling of the mixture, the solid is isolated by filtration, washed with ethanol and ether, and dried (yield 3.7 g). This solid is finely ground in a smooth mortar; 1.00 g is mixed with 500 mL of toluene; the mixture is refluxed for 1 h, and the precipitate is filtered hot and washed with ether (60% yield). TLC shows this to be the β isomer with a small amount of the α isomer and a residue. It is purified by first dissolving in hot acetonitrile (ca. 120 mL), filtering, and adding water (3 volumes). After the mixture is allowed to stand overnight a 73% yield of impure material is obtained. This is dissolved in chloroform and the solution is passed over a short alumina column, which is washed with chloroform. A dark band of residue remains at the top of the column. After evaporation to low volume and addition of diethyl ether, a dark blue crystalline solid is obtained. Anal. Calcd for $[\text{Ru}(\text{Azpy})_2\text{Cl}_2] \cdot \text{CHCl}_3$: C, 41.99; H, 2.91; N, 12.78; Cl, 26.95. Found: C, 42.30; H, 3.04; N, 12.97; Cl, 27.30.

Drying in vacuo at 110 °C for 23 h results in a 19% weight loss. Anal. Calcd for $[\text{Ru}(\text{Azpy})_2\text{Cl}_2]$: C, 49.07; H, 3.37; N, 15.61; Cl, 13.17. Found: C, 49.49; H, 3.62; N, 15.88; Cl, 13.60.

γ - $[\text{Ru}(\text{Azpy})_2\text{Cl}_2]$. A 4-g sample of $[\text{Ru}(\text{Me}_2\text{SO})_4\text{Cl}_2]$ and 3.04 g of Azpy are mixed with 400 mL of acetone, and the mixture refluxed with stirring for ca. 17 h. Upon cooling of the mixture, the green solid is isolated by filtration, washed with acetone and diethyl ether, and dried (75% of crude material). This sample is recrystallized by dissolution in chloroform (250 mL/g) and addition of an equal volume of ether. If TLC shows more than one green spot, the sample is recrystallized again.

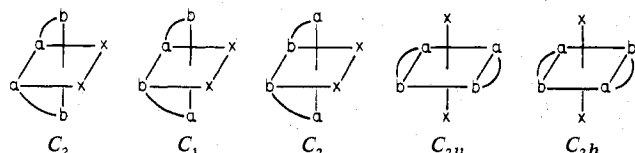
The sample is isolated by filtration as a mass of felted green or purple (larger crystals) needles—this “felting” is unique to the γ isomer. After being washed with diethyl ether, the sample is dried in vacuo over P_4O_{10} . Anal. Calcd for $[\text{Ru}(\text{Azpy})_2\text{Cl}_2]$: C, 49.07; H, 3.37; N, 15.61; Cl, 13.17. Found: C, 48.83; H, 3.81; N, 15.30; Cl, 13.56.

α - $[\text{Ru}(\text{Azpy})_2\text{Cl}_2]$. A 2-g sample of the crude green γ isomer is mixed with 600 mL of xylene, and the mixture is refluxed for ca. 3 h. (TLC shows no green present). When the system is cooled, the complex is isolated by filtration, washed with diethyl ether, and dried in vacuo over P_4O_{10} (yield 85%). This compound appears as small dark blue crystals with a copper luster. It can be recrystallized from chloroform–diethyl ether. Anal. Calcd for $[\text{Ru}(\text{Azpy})_2\text{Cl}_2]$: C, 49.07; H, 3.37; N, 15.61; Cl, 13.17. Found: C, 48.79; H, 3.58; N, 15.80; Cl, 13.64.

Results and Discussion

Refluxing RuCl_3 and Azpy in ethanol gives a mixture containing three principal components when the mole ratio of the reactants is 1:2 or 1:3. All three components are complexes of the formula $[\text{Ru}(\text{Azpy})_2\text{Cl}_2]$; to date we have not isolated a stable tris complex.

With an asymmetric ligand like Azpy, five geometrical isomers of the dichloro bis complex are possible: three cis forms (two of C_2 and one of C_1 symmetry which are diastereomeric) and two trans forms (C_{2v} and C_{2h}). Structures are assigned to the three isomers obtained in the present work.



Upon reflux of the crude reaction mixture in toluene, two isomers are extracted, leaving the β isomer. The α and γ isomers are obtained through a different route; refluxing $[\text{Ru}(\text{Me}_2\text{SO})_4\text{Cl}_2]$ with Azpy in acetone again gives all three

Table I. Kinetics Parameters, $\gamma \rightarrow \alpha^a$

T, K	$10^{-5}k, \text{s}^{-1}$	T, K	$10^{-5}k, \text{s}^{-1}$
414	7.9 ± 0.7	393	0.85 ± 0.05
403	2.6 ± 0.5		

$$^a \Delta E_a = 34 \pm 1 \text{ kcal}; \Delta H^\ddagger = 33 \pm 1 \text{ kcal}; \Delta S^\ddagger = 1 \pm 0.2 \text{ eu.}$$

forms. However, the green γ isomer is of lower solubility in this solvent than the other forms and is obtained in high yield. This reaction is noteworthy in that Evans et al.¹¹ found complete substitution of Me_2SO to generally occur only by running reactions in neat ligand and never in a solvent. We conclude that Azpy must be an excellent trans-labilizing ligand (better than bpy) for this reaction to proceed to completion at the temperature of refluxing acetone.

Both β and γ forms isomerize to some extent to the α isomer. Isomerization of the β isomer is detectable after 7 days in refluxing toluene. The γ form will isomerize in the solid state (several days at 170 °C), but it will do so more rapidly in solvents. We have briefly investigated the kinetics of the $\gamma \rightarrow \alpha$ isomerization. Preparation of the α isomer proceeds most conveniently by isomerization of the γ isomer in refluxing xylene.

^{13}C NMR analysis immediately gives the structure of the β isomer as the cis complex of C_1 symmetry. All other isomers have at least a twofold axis and only nine lines are anticipated; this is observed for the α and γ forms. In the ^{13}C spectrum of the β isomer, we find 18 lines, indicating the lack of any symmetry element in the complex.

From infrared data (below) we conclude the γ isomer structure to be trans (C_{2h}). Thus, the most stable α form is either one of the cis (C_2) or trans (C_{2v}) isomers. We feel the trans (C_{2v}) structure would be the least stable. In this structure there would be cis coplanar pyridine rings; it is generally concluded that this is an unstable configuration.¹² Furthermore, the visible spectra of α and β isomers are much more alike than the α and γ forms; from these considerations we take it that the α isomer has the cis (C_2) configuration.

Kinetics. In order to gain some insight into the isomerization process, we briefly investigated the rate of conversion of the γ to the α isomer. Between 120 and 141 °C in *m*-dichlorobenzene the reaction followed first-order kinetics. We were unable to study the solvent dependence due to a lack of suitable solvents—those with high boiling point, in which the γ isomer is sufficiently soluble for spectrophotometric accuracy, not giving a solvent substitution product. Kinetic parameters are included in Table I.

From the temperature-dependence data we calculate ΔS^\ddagger to be ca. 1 eu. This implies a nondissociative isomerization mechanism. For a C_{2h} species to convert to a C_2 , a simple “edge twist” mechanism suffices, i.e., one Cl^- and one end of Azpy interchanging positions by rotation about an imaginary twofold axis through the octahedral edge connecting them.

Further work, particularly with a larger variety of substituted compounds of the $[\text{Ru}(\text{Azpy})_2\text{X}_2]$ type, should be very informative.

Infrared Spectra. Our objectives in studying the IR spectra were to locate the $\text{N}=\text{N}$ mode, identify the $\text{Ru}-\text{L}$ stretching modes, and symmetry where possible. The $\text{N}=\text{N}$ stretching vibration has been observed near 1420 cm^{-1} in some first-row complexes of azopyridine.¹³ In general, the $\text{N}=\text{N}$ stretching mode appears near 1420 cm^{-1} when conjugated and asymmetric (IR allowed).¹⁴ We find a strong absorption for Azpy

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Table II. Infrared Bands in the 1600–1300-cm⁻¹ Region^a

assignt	Azpy	α	β	γ
Ph-I, py-I	1587 sh	1600 m	1603 m	1600 m
Ph-II, py-II } }	1584 s	1589 m	1591 w	1585 sh
	1578 m			
	1498 sh			
Ph-III	1495 m	1482 m	1485 m	1485 m
py-III	1479 s	1456 m	1478 w, sh	1466 m
	1466 m			
Ph-IV	1453 m	1451 s	1454 s	1453 m
py-IV	1443 m	1437 m	1444 w, sh	1445 sh
	1428 sh			
N=N (free Azpy)	1424 vs			
		1368 m		1380 vw
		1336 m	1337 m	1330 m
N=N (complex)		1353 m		1314 m
		1310 m		1303 s
N=N (complex)		1295 m	1298 s	1290 s
		1295 s	1298 s	

^a Key: s, strong; m, medium; w, weak, v, very; sh, shoulder.

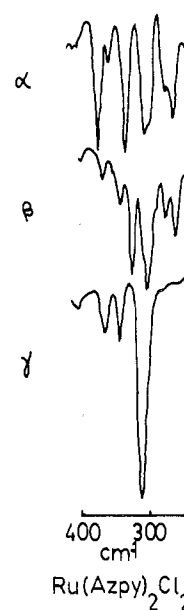
Table III. Infrared Bands in the 400–250-cm⁻¹ Region

assignt	Azpy	α	β	γ
Ru-N(py)		268 s	265 m	
Ru-N(azo)		280 m	279 m	
		304 sh	290 sh	
Ru-Cl (C_1 , C_2)		308 s	306 s	
			310 sh	
Ru-Cl (C_{2h})				315 vs
Ru-Cl (C_1 , C_2)		336 s	328 s	
Ru-N(py)		358 m	346 m-w	346 m
Ru-N(azo)		376 s	371 w	368 m
ligand	403 w	405 vw	400 vw	405 vw

at 1424 cm⁻¹ (Table II) which we assign to this mode. However, this band has shifted in the complexes. To locate it, we first assign the ring modes for 2-substituted pyridine and monosubstituted benzene between 1600 and 1400 cm⁻¹,¹⁴ which accounts for all major bands in this region. Since all observed bands are accounted for, we look below 1400 cm⁻¹ for the azo mode, in particular looking for a strong band which does not correspond with one in the free ligand. We find a band in the complexes between 1290 and 1298 cm⁻¹ meeting these requirements which we assign as an azo stretching mode. However, an additional strong band appears in all three isomers between 1303 and 1323 cm⁻¹; in the α and β compounds these are located in the region where free Azpy has a medium-weak band. In addition to complexed azo linkage shifting to lower energy by 100 cm⁻¹, the mode appears to have split, possibly due to coupling of the ligand bands through the metal.

An azo mode at 1424 cm⁻¹ (free Azpy) indicates conjugation;¹⁴ the shift to lower energy in the complexes indicates less double-bond character in the N=N group. This is strong evidence for substantial π bonding to ruthenium through an azo nitrogen. As the Ru-N bond order increases incorporating more π bonding, the N-N bond order must decrease. Low azo stretching frequencies have been observed in iron(II) complexes; Raghavendra and Chakravorty observe this mode at 1353 cm⁻¹ in Fe(Azpy)₃²⁺.⁸ Baldwin et al.¹³ observe it at 1393 cm⁻¹ in an iron(II) azopyridine complex. Other azopyridine complexes¹³ and Ni(II)-Azpy complexes⁸ have the azo stretching mode in the anticipated region (ca. 1420 cm⁻¹). It remains to be seen whether this lowering (and substantial π bonding) is characteristic of only d⁶ complexes.

In the 1600–1400-cm⁻¹ region, pyridine and benzene ring modes appear as they should. Ring III (benzene; "semicircle stretching" mode) is located at 1495 cm⁻¹ in free Azpy. A shift in the complexes (1482–1485 cm⁻¹) is in agreement with the effect of electron-withdrawing substituents.¹⁴ Thus, the locations of both the azo mode and benzene ring III indicate

Figure 1. Infrared spectra of Ru(Azpy)₂Cl₂ isomers in the CsBr region.Table IV. IR-Allowed Modes for [Ru(Azpy)₂Cl₂]

isomer sym	IR-active modes (str)		
	Ru-Cl	Ru-py	Ru-azo
C_1	2 A	2 A	2 A
C_2	A + B	A + B	A + B
C_{2v}	A ₁ + B ₁	A ₁ + B ₂	A ₁ + B ₂
C_{2h}	A _u	B _u	B _u

electron withdrawal from the ligand.

Table III lists IR data and band assignments in the low-energy spectral region; this region is shown in Figure 1. Assignments of metal-ligand modes are hampered by a lack of extensive data; however, a few generalizations can be made. Ru(pyridine)₆(BF₄)₂ has a Ru-N stretching mode at 326 cm⁻¹,¹⁵ while metal-bpy modes (for d⁶ metals) appear between 400 and 300 cm⁻¹.¹⁶ Staniewicz et al. assign the Ru-N stretch in Ru(bpy)₃²⁺ at 338 and 326 cm⁻¹.¹⁷ We anticipate the Ru-Azpy stretch in this region.

A number of workers have assigned Ru-Cl stretching modes in this region: for [Ru(Me₂SO)₄Cl₂] they are at 330 and 325 cm⁻¹,¹¹ for [Ru(bpy)₂Cl₂] they are at 338 and 319 cm⁻¹,¹⁸ and the strong band appearing at 310 cm⁻¹ in K₃[RuCl₆] is most certainly Ru^{III}-Cl.¹⁹ Thus, we look for Ru-Cl near 330 cm⁻¹.

Both the β isomer (C_1) and the α isomer (C_2) should have two IR-active Ru-Cl stretching modes and four IR-active Ru-N stretching modes (Table IV). These two compounds show a 1:1 correspondence in the number of peaks and approximate locations in this region. The two strong bands near 308 and 330 cm⁻¹ are assigned as Ru-Cl in accord with previous work. The four bands near 375, 350, 280, and 265 cm⁻¹ are assigned as Ru-N stretching modes. If the γ isomer were either C_2 or C_{2v} , it should also have two Ru-Cl and four Ru-N stretching modes; C_{2h} however, would have half as many. This is exactly what we find, only one band for Ru-Cl (315 cm⁻¹) and two in the region anticipated for Ru-N (368 and 346 cm⁻¹). Thus, we conclude the γ isomer to be of C_{2h} symmetry (the trans-trans structure).

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Table V. Visible Spectra of Ru(Azpy)₂Cl₂ Isomers

isomer	λ_{\max} , nm ($\epsilon \times 10^{-4}$) ^a		
α (solid) ^b	586	470	392
α (CHCl ₃)	588 (1.14)	465 (0.203)	320 (2.50)
α (<i>m</i> -Cl ₂ Ph)	598 (1.14)	476 (0.225)	324 (2.67)
α (Me ₂ SO)	588 (1.14)	468 (0.206)	320 (2.49)
β (solid) ^b	568	490 sh	387
β -CHCl ₃ (solid) ^b	560	480 sh	400
β (CHCl ₃)	577 (1.07)	485 sh	338 (1.80)
β (<i>m</i> -Cl ₂ Ph)	587 (1.08)	495 sh	338 (2.01)
β (Me ₂ SO)	574 (1.10)	480 sh	330 (2.00)
γ (solid) ^b	620	450	400 sh
γ (CHCl ₃)	632 (1.20)	408 (0.958)	300 (1.53)
γ (<i>m</i> -Cl ₂ Ph)	644 (1.14)	408 (0.963)	<300
γ (Me ₂ SO)	644 (1.23)	404 (0.963)	<300

^a Molar extinction coefficient. ^b Results by photoacoustic spectroscopy.

As more derivatives become characterized, we hope to further support these assignments.

Visible Spectra. Table V lists the results obtained on examining the visible spectra of these complexes. Large values for the molar extinction coefficient (ca. 10⁴) indicate the absorption bands to be of charge-transfer origin, a conclusion generally held valid in Ru-bpy complexes.²⁰ While the α and β isomers have quite similar spectra, the γ form has a spectrum substantially shifted, further supporting the concluded structural differences. Some solvent dependence is observed, with maxima location shifting with solvent.

No photoluminescence could be detected from these complexes. Irradiating with a nitrogen laser at 7 K gave no indication of emission between 400 and 800 nm. [Ru(bpy)₂Cl₂] is reported to emit near 770 nm.²⁰ Since the [Ru(Azpy)₂Cl₂] isomers absorb at somewhat lower energy than this compound, it is possible that emission is occurring but beyond the detection limits of our equipment. Krug and Demas have proposed that only an α -diimine functionality is necessary for charge-transfer emission from ruthenium(II) complexes.²¹ The pronounced lowering of double-bond character in the N=N linkage we have observed could be eliminating the possibility of luminescence in the Ru-Azpy complexes by removing the α -diimine functionality.

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Table VI. Cyclic Voltammetry

complex	$E_{1/2}$, ^a V	Δ , ^b mV
α -[Ru(Azpy) ₂ Cl ₂]	1.21	96
β -[Ru(Azpy) ₂ Cl ₂]	1.15	96
γ -[Ru(Azpy) ₂ Cl ₂]	1.00	100

^a Reported values are for reduction of the generated ruthenium(III) complex, vs. the SCE at ca. 25 °C. They are the average of anodic and cathodic cyclic voltammogram peaks.

^b Experimental peak separation. Ru(bpy)₃(ClO₄)₂ under identical conditions shows Δ of 115 mV.

Cyclic Voltammetry. Cyclic voltammetry on dichloromethane solutions was studied in order to determine redox potentials of the complexes (Table VI). Although the forward and reverse peaks were separated by 90–100 mV, there was no peak shift on repeated sweeps nor change in current intensity; peak separation is less than in the reversible Ru(bpy)₃²⁺ couple. Thus, the couples are reversible.

Two points are brought out by these data: First, the $E_{1/2}$ potentials are in the same order as the observed stabilities of the isomers, the α isomer being the most stable to oxidation. This is consistent with the other observations we have made on these compounds.

Second, Azpy appears to be a better ligand for stabilizing ruthenium(II) than bpy. While Ru(bpy)₃²⁺ has $E_{1/2}$ of 1.29 V (in CH₃CN vs. the SSCE),²² substituted complexes (e.g., [Ru(bpy)₂X₂]) have lower values, with [Ru(bpy)₂Cl₂] having $E_{1/2}$ of 0.30 V (CH₃CN vs. the SSCE).²³ It is this last compound with which one must compare [Ru(Azpy)₂Cl₂]; our higher values indicate considerably greater oxidative stability than that for the bpy analogue. This is, again, strong evidence for pronounced d π -p π interaction in [Ru(Azpy)₂Cl₂].

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Registry No. α -[Ru(Azpy)₂Cl₂], 73926-31-5; β -[Ru(Azpy)₂Cl₂], 74006-30-7; γ -[Ru(Azpy)₂Cl₂], 73952-48-4; Azpy, 2569-57-5; 2-aminopyridine, 504-29-0; nitrosobenzene, 586-96-9; [Ru(Me₂SO)₄Cl₂], 11070-19-2.

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