

## The Use of Carbon-13 NMR Spectroscopy to Differentiate Between *Cis*- and *Trans*- Isomers of $Rh(en)_2XY^{n+}$

F. P. JAKSE, J. V. PAUKSTELIS and J. D. PETERSEN

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, U.S.A.

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*Carbon-13 magnetic resonance spectroscopy is shown to be a viable tool in differentiating geometric isomers of the type, cis- and trans- $Rh(en)_2XY^{n+}$ . The  $Rh(en)_3^{3+}$  ion and the trans- $Rh(en)_2XCl^{n+}$  ions (where  $X = Cl, OH_2$  and  $NH_3$ ) display only one proton-decoupled C-13 signal. The cis complex ions, cis- $Rh(en)_2XCl^{n+}$ , display between two ( $X = Cl$ ) and four ( $X = OH_2, NH_3$ )  $^{13}C$  peaks. The configurational changes of the individual chelate rings ( $\lambda \rightleftharpoons \delta$ ) appear to be fast on the nmr time scale. The splitting pattern and chemical shifts have enabled us to assign a cis configuration to the  $Rh(en)_2(enH)Cl^{3+}$  product formed from photolysis of  $Rh(en)_3^{3+}$  in 1M HCl. The results reported herein will be compared and contrasted to earlier synthetic and  $^{13}C$  nmr studies.*

### Introduction

Numerous techniques, including selective precipitation [1], electronic absorption spectra [2–4], infrared spectroscopy [3–6] and nuclear magnetic resonance spectroscopy [7–9], have been employed to differentiate between *cis*- and *trans*-bis(ethylenediamine) complexes of Co(III) and Rh(III). Of these techniques [1–9], carbon-13 nmr spectroscopy [8] has proved to be very effective in configurational studies of compounds of the type, *cis*- or *trans*- $Co(en)_2XY^{n+}$ . The ensuing application of  $^{13}C$  techniques to the homologous Rh(III) complexes [9],  $Rh(en)_2XY^{n+}$ , gave ambiguous results which were not as readily interpreted as the spectra of the Co(III) complexes [7].

Recently, we have been preparing compounds of the type  $Rh(en)_2XY^{n+}$  and have found that some of our complexes, especially *cis*- $Rh(en)_2Cl_2^+$ , have electronic spectra which have different molar extinction coefficient values than those previously described in the literature [3, 10, 11]. The large discrepancy in the  $\epsilon$  value of *cis*- $Rh(en)_2Cl_2^+$  creates a problem in evaluating the validity of the many photochemical [12, 13] and thermal studies [3, 4, 14–18] using this complex when prepared as previously reported. In addition, the ambiguous results [9] ob-

tained from carbon-13 nmr spectra of Rh(III) complexes mainly centered around interpretation of the spectrum of *cis*- $Rh(en)_2Cl_2^+$ .

We felt that the conflicting electronic spectra results on *cis*- and *trans*- $Rh(en)_2XY^{n+}$  complexes warranted a reinvestigation of  $^{13}C$  nmr spectroscopy as a method for delineating *cis* and *trans* geometric isomers. Reported herein are the results of that investigation.

### Experimental

#### Syntheses

The tris(ethylenediamine)rhodium(III) complex  $[Rh(en)_3]Cl_3 \cdot 3H_2O$  was prepared by the standard literature procedure [19].

*cis*- and *trans*- $[Rh(en)_2Cl_2]NO_3$  and *cis*- and *trans*- $[Rh(en)_2(NH_3)Cl](NO_3)_2$

The nitrate salts of the two dichlorobis(ethylenediamine) and the two chloroamminebis(ethylenediamine)rhodium(III) complex were prepared as previously described [10].

*cis*- $[Rh(en)_2Cl_2]ClO_4$

Conversion of the nitrate salt of the *cis*-dichloro complex into the corresponding perchlorate salt was accomplished by a reprecipitation technique. 0.15 grams of the nitrate salt was dissolved in a minimum of hot water and the solution was filtered directly into 5 ml of methanol which had been saturated with sodium perchlorate. After cooling for one hour, the yellow crystals were collected, washed with ethanol then ether, and dried under vacuum. Initial recovery of the complex corresponded to 70% yield.

*trans*- $[Rh(en)_2(OH_2)Cl](ClO_4)_2$

The literature procedure [11] with minor modifications was used to prepare *trans*- $[Rh(en)_2(OH_2)Cl](ClO_4)_2$ . A 0.42 g (0.89 mmol) sample of *trans*- $[Rh(en)_2Cl_2]ClO_4$  was digested with a solution of  $AgClO_4$  (0.93 mmol) (prepared from 0.115 g of  $Ag_2O$  dissolved in a minimum of concentrated  $HClO_4$ ) and

diluted to 5 ml. The solution was refluxed for 2.5 hours, cooled to room temperature, and filtered to remove the white, AgCl precipitate. The filtrate was rotary-evaporated to a golden yellow oil with pale yellow crystals appearing after the addition of ethanol. The collected crystals were washed with ethanol then ether and dried under vacuum. A second crop was obtained by rotary-evaporation of the final filtrate. The total yield was 70.5%.

*cis*-Rh(en)<sub>2</sub>(OH<sub>2</sub>)Cl<sup>2+</sup>

0.036 g, 0.092 mmol of *cis*-[Rh(en)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub> was digested with a solution of AgClO<sub>4</sub> (0.046 mmol) in 2 ml of H<sub>2</sub>O and 2 ml of D<sub>2</sub>O. The solution was refluxed for 2 hours, cooled to room temperature, and filtered to remove the AgCl solid. The resulting filtrate was used directly to obtain the carbon-13 magnetic resonance spectra of *cis*-Rh(en)<sub>2</sub>(OH<sub>2</sub>)Cl<sup>2+</sup>.

*cis*-[Rh(en)<sub>2</sub>(enH)Cl]Cl<sub>3</sub>·2H<sub>2</sub>O

0.5 g, 1.1 mmol of [Rh(en)<sub>3</sub>]Cl<sub>3</sub>·3H<sub>2</sub>O was dissolved in 35 ml of deoxygenated 1 F HCl. The solution was placed into a quartz tube and irradiated at ~5 °C for 4 days with three low pressure mercury lamps (Ultraviolet Industries, PCQ-XI). The solution was cooled with a fan and stirred with a magnetic stirring bar throughout the photolysis.

The photolysis was considered complete when the absorption band at 301 nm (Rh(en)<sub>3</sub><sup>3+</sup>) had reached a minimum with respect to the 345-nm band of the

photoproduct. The solvent was removed from the system by rotary evaporation leaving a solid which was predominately photoproduct with a small amount of starting material. If irradiation is continued for longer periods of time to try to minimize the amount of unreacted starting material, Rh(en)<sub>3</sub><sup>3+</sup>, a loss in absorbance at 345 nm and an increase in absorbance at 406 nm results. Ion exchange chromatography (Dowex 50W X-4) and electronic spectroscopy [16] indicated that the increased absorbance at 406 nm was due to a secondary reaction resulting in the formation of *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>. Isolation of reasonably pure *cis*-[Rh(en)<sub>2</sub>(enH)Cl]-Cl<sub>3</sub>·2H<sub>2</sub>O was accomplished by minimizing the secondary processes and recrystallizing from 1 F HCl (photoproduct more soluble in 1 F HCl than Rh(en)<sub>3</sub><sup>3+</sup>). *Anal.* Calcd for C<sub>6</sub>H<sub>13</sub>N<sub>6</sub>Cl<sub>4</sub>Rh·2H<sub>2</sub>O: C, 15.6%; H, 6.3%; N, 18.2%; Cl, 30.7%. Found: C, 15.6%; H, 6.4%; N, 18.4%; Cl, 32.8%.

The electronic absorption spectra and molar extinction coefficients for all of the complexes described above appear in Table I.

*Nuclear Magnetic Resonance Spectra*

Carbon-13 nmr spectra were obtained with a Varian XL-100-15 spectrometer operating at a frequency of 25.2 MHz and equipped with a Nicolet TT-100 Data System with quadrature phase detection and 20K of memory, allowing 16K data points, 8K points in the frequency domain for 3012 Hz spectra

TABLE I. Electronic Spectra of Rh(III) Complexes.

Compound	$\lambda_{\max}$ , nm	$\epsilon_{\max}$ , M <sup>-1</sup> cm <sup>-1</sup>
[Rh(en) <sub>3</sub> ]Cl <sub>3</sub>	301 255	243(238) <sup>a</sup> 194(191) <sup>a</sup>
<i>trans</i> -[Rh(en) <sub>2</sub> Cl <sub>2</sub> ]NO <sub>3</sub>	406 286	83 (75) <sup>b</sup> 134(130) <sup>b</sup>
<i>trans</i> -[Rh(en) <sub>2</sub> (OH <sub>2</sub> )Cl](ClO <sub>4</sub> ) <sub>2</sub>	386(383) <sup>c</sup> 282(238) <sup>c</sup>	55 (46) <sup>c</sup> 147(143) <sup>c</sup>
<i>trans</i> -[Rh(en) <sub>2</sub> (NH <sub>3</sub> )Cl](NO <sub>3</sub> ) <sub>2</sub>	342 275	80 (95) <sup>b</sup> 113(120) <sup>b</sup>
<i>cis</i> -[Rh(en) <sub>2</sub> Cl <sub>2</sub> ]NO <sub>3</sub> <sup>d</sup>	352 295	147(155) <sup>b</sup> 189(180) <sup>b</sup>
<i>cis</i> -[Rh(en) <sub>2</sub> Cl <sub>2</sub> ]ClO <sub>4</sub>	352 295	203 205
<i>cis</i> -[Rh(en) <sub>2</sub> (OH <sub>2</sub> )Cl]	325 282	e e
<i>cis</i> -[Rh(en) <sub>2</sub> (NH <sub>3</sub> )Cl]	342 276	150 <sup>b</sup> 195 <sup>b</sup>
<i>cis</i> -[Rh(en) <sub>2</sub> (enH)Cl]Cl <sub>3</sub>	345 274	140 239

<sup>a</sup>Reference 19. <sup>b</sup>Reference 3. <sup>c</sup>Reference 11. <sup>d</sup>Contaminated with *trans*-[Rh(en)<sub>2</sub>Cl<sub>2</sub>]NO<sub>3</sub> (see text). <sup>e</sup>The complex is extremely soluble in aqueous solution so the complex was never isolated. The nmr spectra was recorded on complexes prepared *in situ*.

width. All spectra were measured in  $\text{D}_2\text{O}/\text{H}_2\text{O}$  (1:1, v/v) mixtures at concentrations varying between 0.05 and 0.3M depending on the solubility of the complex. The flip angle was varied between 40 and 60° with a 7 second delay between pulses. The number of pulses required to obtain a good signal-to-noise ratio was concentration dependent and varied from 512 to 13,992.

The deuterium resonance of  $\text{D}_2\text{O}$  was used as the lock signal. Carbon-13 chemical shifts were measured relative to internal dioxane but are reported relative to external TMS. The conversion to external TMS was calculated with the relationship:

$$\delta_{\text{ext TMS}} = \delta_{\text{int dioxane}} + 67.40 \text{ ppm}$$

Spectral reproducibility was  $> \pm 0.03$  ppm.

## Results and Discussion

The electronic spectra of all of the complexes reported in this study are listed in Table I. All of the transitions can be assigned as ligand field transitions derived from the  $^1\text{T}_1 \leftarrow ^1\text{A}_1$  and  $^1\text{T}_2 \leftarrow ^1\text{A}_1$  transitions in the octahedral environment. The complexes used in this study, with one notable exception, have absorption maxima and molar extinction coefficients which are consistent with literature values. The one exception occurs when the  $\text{cis-Rh}(\text{en})_2\text{Cl}_2^+$  complex ion is recrystallized as the perchlorate salt rather than the customarily used nitrate or chloride salt. The wavelength maxima (352 and 295 nm) are the same for all anions, but the extinction coefficients are 203 and  $205 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively, for the perchlorate salt which differ from the literature values [3] of 155 and  $180 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively, for the nitrate salt. In addition, the nitrate salt of  $\text{cis-Rh}(\text{en})_2\text{Cl}_2^+$  has a larger  $\epsilon$  value at 406 nm (the maximum of  $\text{trans-Rh}(\text{en})_2\text{Cl}_2^+$ ) than the corresponding perchlorate salt. Since the *cis* and *trans* isomers of  $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{NO}_3$  are prepared together and separated by solubility differences, there is a high probability that the isolated salts will be contaminated with the other geometric isomer. Assuming that the perchlorate salt is pure *cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{ClO}_4$ , calculations from the absorption spectra of *cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{NO}_3$  indicate that the nitrate salt, believed to be the *cis* isomer [3, 10], is actually an 80%/20% mixture of the *cis/trans* geometric isomers. This result based on the electronic absorption spectra will be confirmed by  $^{13}\text{C}$  nmr in the following discussion.

The chemical shifts of the proton-decoupled carbon-13 magnetic resonance spectra for all complexes in this study are listed in Table II with selected spectra appearing in Figures 1–5. The compounds in Figures 2–5 are drawn in the  $\Lambda$  configuration. In reality, a racemic mixture of  $\Lambda$  and  $\Delta$  forms are present. However, since enantiomeric pairs (*e.g.*,

TABLE II. Carbon-13 Chemical Shifts of Rh(III) complexes.

Compound	$\delta$ ( $^{13}\text{C}$ ), ppm <sup>a</sup>
$\text{Rh}(\text{en})_3^{3+}$	46.36
<i>trans</i> - $\text{Rh}(\text{en})_2\text{Cl}_2^+$	45.68
<i>trans</i> - $\text{Rh}(\text{en})_2(\text{OH}_2)\text{Cl}^{2+}$	45.75
<i>trans</i> - $\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}^{2+}$	45.64
<i>cis</i> - $\text{Rh}(\text{en})_2\text{Cl}_2^+$	47.25 46.15
<i>cis</i> - $\text{Rh}(\text{en})_2(\text{OH}_2)\text{Cl}^{2+}$	47.78 47.07 45.98 45.20
<i>cis</i> - $\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}^{2+}$	47.07 46.27 45.81(2) <sup>b</sup>
<i>cis</i> - $\text{Rh}(\text{en})_2(\text{enH})\text{Cl}^{3+}$	47.15 46.56 45.99
	45.94 43.30 40.59(br)

<sup>a</sup>Chemical shifts reported vs. TMS with dioxane (67.40 ppm) as an internal reference. <sup>b</sup>Peak height corresponds to two carbons, but individual peaks were not resolvable.

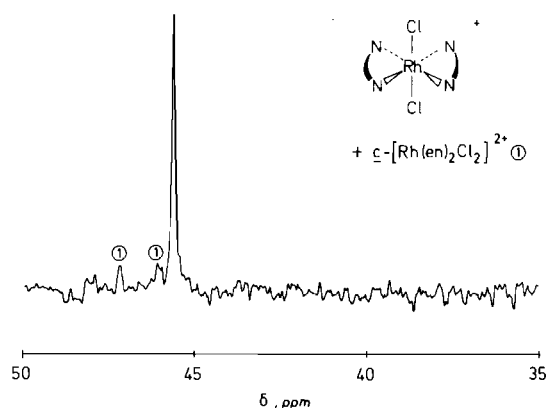


Figure 1. Proton-decoupled C-13 spectra of *trans*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ .

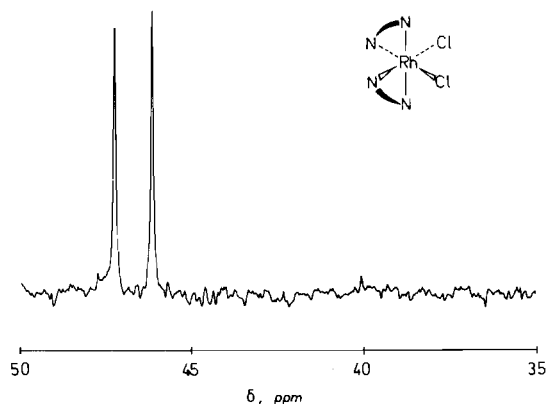


Figure 2. Proton-decoupled C-13 spectra of *cis*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ .

$\Lambda\delta\delta\delta$  and  $\Delta\lambda\lambda\lambda$ ) yield identical carbon-13 spectra, we will limit the ensuing discussion on the tris complex and the *cis*- $\text{Rh}(\text{en})_2\text{XY}^{n+}$  complexes to the  $\Lambda$  form.

The proton-decoupled  $^{13}\text{C}$  spectra of  $\text{Rh}(\text{en})_3$  [3] and the *trans* complexes, *trans*- $\text{Rh}(\text{en})_2\text{XCl}^{n+}$  (where X = Cl,  $\text{OH}_2$  and  $\text{NH}_3$ ), exhibit only one signal for each complex (Table II). For  $\text{Rh}(\text{en})_3^{3+}$ , this peak

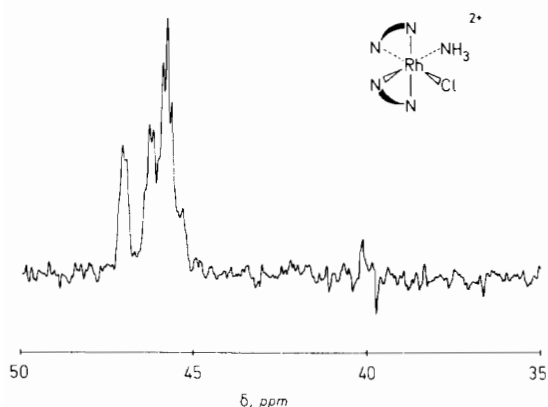


Figure 3. Proton-decoupled C-13 spectra of *cis*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)Cl<sub>2</sub><sup>2+</sup>.

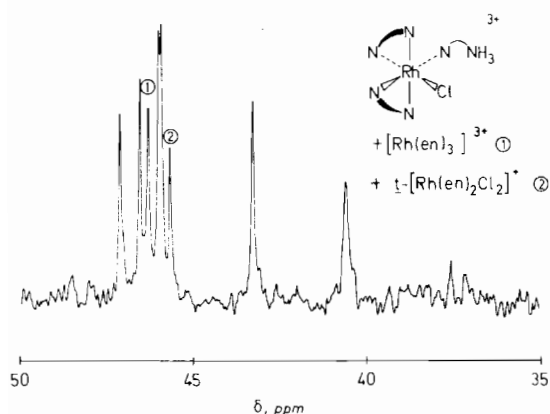


Figure 4. Proton-decoupled C-13 spectra of *cis*-Rh(en)<sub>2</sub>(enH)Cl<sub>3</sub><sup>3+</sup> with *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> and Rh(en)<sub>3</sub><sup>3+</sup> contaminants.

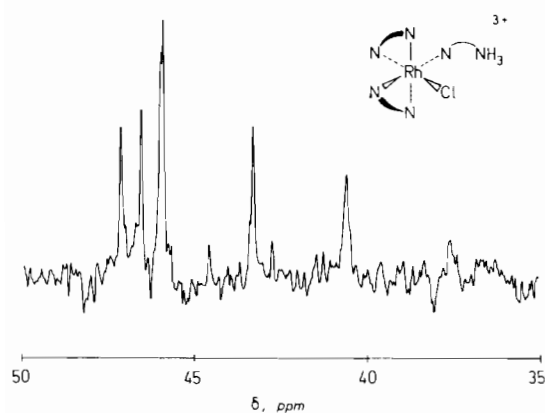


Figure 5. Proton-decoupled C-13 spectra of *cis*-Rh(en)<sub>2</sub>(enH)Cl<sub>3</sub><sup>3+</sup> after computer subtraction of contaminants.

appears at 46.36 ppm (*vs.* TMS). Sudmeier and Blackmer [20] have proposed that the equilibrium population of  $\Lambda$ -Rh(en)<sub>3</sub><sup>3+</sup> at 25 °C is ~92%  $\delta\delta\lambda$  and ~8%  $\delta\delta\delta$  from the <sup>1</sup>H nmr spectrum. In terms of the individual chelate rings, these data correspond to ~70%  $\delta$  rings and ~30%  $\lambda$  rings. The presence of only

one peak indicates that either ring conformational changes are rapid on the nmr time scale leading to a coalescence to a single peak or that the peak separations between the  $\Lambda$ - $\delta\delta\lambda$  and  $\Lambda$ - $\delta\delta\delta$  forms are less than the 1 Hz resolution of the spectrometer. The coalescence explanation is strengthened by the calculations of Sudmeier and Blackmer [20] which indicate a small free energy difference of ~1.4 kcal/mol between the  $\Lambda$ - $\delta\delta\lambda$  and  $\Lambda$ - $\delta\delta\delta$  configurations.

The single peaks in the spectra of the *trans*-Rh(en)<sub>2</sub>XCl<sup>n+</sup> complexes appear at 45.68, 45.75 and 45.64 ppm for X = Cl, OH<sub>2</sub> and NH<sub>3</sub>, respectively. Unlike the tris complex [21], there are only two possible configurations for the two ethylenediamine ligands in these complexes. Corey and Bailar [22] have suggested that the  $\lambda\lambda$  and  $\delta\delta$  forms are ~1.0 kcal/mol lower in energy than the  $\lambda\delta$  and  $\delta\lambda$  forms. This structural preference results from the position of the amine protons which are eclipsed in the  $\lambda\delta$  and staggered in the  $\lambda\lambda$  and  $\delta\delta$  forms [23]. This assumed free energy difference corresponds to an 85:15 mixture of  $\lambda\lambda$  (and  $\delta\delta$ ) to  $\delta\lambda$  forms [24]. Rough calculations using coalescence equations [25] indicate that for the nmr signals of the different conformers to be within 10 ppm of each other (an extreme upper limit considering the similarity of structures), the activation energy must be at least 14 kcal/mol. This value seems unreasonably high and indicates that the signal observed at room temperature is the configurational average.

The single carbon-13 resonance signal observed for each *trans*-Rh(en)<sub>2</sub>XCl<sup>n+</sup> complex ion is relatively insensitive to the nature of X. The values of 45.68, 45.75 and 45.64 ppm, respectively, for X = Cl, OH<sub>2</sub>, and NH<sub>3</sub> reflect differences that are larger than the spectral reproducibility of  $\pm 0.03$  ppm but all fall within 0.11 ppm. The small changes of the chemical shifts, due to the variation of X group *cis* to be ethylenediamine ligand, arise from electronic changes in the Rh-X bond and changes in the remote anisotropic screening due to X and must be either small for both effects or be cancelling influences on the <sup>13</sup>C shifts. This insensitivity to changes in the nature of groups bound *cis* to ethylenediamine ligands is also observed in the carbon-13 magnetic resonance of *trans*-Co(en)<sub>2</sub>XY<sup>n+</sup> complex ions [8], where the single carbon resonances appear at 46.0 ppm (X = Y = Cl), 45.7 ppm (X = Y = NO<sub>2</sub>), 46.0 ppm (X = Y = NCS), and 46.0 ppm (X = Cl, Y = NCS).

The carbon-13 chemical shifts of the *cis* complexes, *cis*-Rh(en)<sub>2</sub>XCl<sup>n+</sup> (where X = Cl, OH<sub>2</sub>, NH<sub>3</sub>, and enH (NH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>3</sub><sup>+</sup>)), are given in Table II. Once again, we see no multiple peaks which can be assigned as  $\lambda$  and  $\delta$  ring conformational differences. The most symmetrical *cis* complex, *cis*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, can exist in three chemically non-equivalent forms. Using the  $\Lambda$  isomer as a model, the

ethylenediamine ligands can exist in the  $\lambda\lambda$ ,  $\lambda\delta$  or  $\delta\delta$  conformation, which have 2, 4 and 2 non-equivalent carbon atoms, respectively. Thus, unlike the *trans* isomers where two forms are in equilibrium, the *cis* isomer has three forms of different energy in equilibrium. We do feel, however, that the difference in energy between the  $\lambda\lambda$ ,  $\lambda\delta$  and  $\delta\delta$  conformations is on the order of 1-3 kcal/mol and that the chemical shifts will only vary by a maximum of a few ppm; so that the nmr experiment will only display the average configurational resonance signal. Similar behavior is observed for the cobalt homologs [8], *cis*- $\text{Co}(\text{en})_2\text{XY}^{n+}$ , with two exceptions. The *cis*- $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$  complex might be expected to show four  $^{13}\text{C}$  signals; however, only three are observed [8]. These data may in fact be the result of a coincidence of two of the signals [26]. A more complicated system to interpret is that of *cis*- $\text{Co}(\text{en})_2(\text{pyridine})\text{Cl}^{2+}$  where five signals are observed rather than the four which would be expected from rapid interconversion of  $\lambda$  and  $\delta$  ring conformations. In this case, perhaps the bulky nature of the pyridine ligand is preventing the rapid interconversions between  $\lambda$  and  $\delta$  configurations. The size of the carbon-13 peaks would then reflect the Boltzmann population of the conformer [26].

Table II contains chemical shift data for *cis*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ , isolated as both the chloride and perchlorate salts. The spectrum of the nitrate salt is virtually identical to the spectrum reported recently for this complex [9]. The three signals previously reported [9] as being the result of slow  $\lambda \rightleftharpoons \delta$  interconversions on the nmr time scale are unequivocally due to a mixture of *cis*- and *trans*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ . Not only does the upfield signal in the sample of *cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{NO}_3$  have a chemical shift identical to that of *trans*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ , but this signal can be enhanced by spiking the sample with *trans*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ , and will disappear when the nitrate salt is recrystallized as the perchlorate salt (Fig. 2). A rough calculation of the relative intensities of the signals for the nitrate salt, indicate that the *trans* impurity makes up about 20% of the sample. This impurity level is consistent with the previously discussed calculations from the electronic spectra. Furthermore, if we reexamine the  $^{13}\text{C}$  nmr spectrum of the *trans* isomer (Fig. 1) we see that a small amount of *cis* complex appears as an impurity in *trans*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{NO}_3$ .

The proton-decoupled  $^{13}\text{C}$  spectra of *cis*- $\text{Rh}(\text{en})_2(\text{OH}_2)\text{Cl}^{2+}$  and *cis*- $\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}^{2+}$  each display signals assignable to four carbon atoms. The chemical shifts for the carbon atoms in *cis*- $\text{Rh}(\text{en})_2(\text{OH}_2)\text{Cl}^{2+}$  appear at 47.78, 47.07, 45.98 and 45.20 ppm. The spectrum of *cis*- $\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}^{2+}$  (Fig. 3) contains only three resolvable signals at 47.07, 46.27 and 45.81 ppm; however, the peak at 45.81 ppm is approximately twice the size of the other two peaks

and no doubt reflects a coincidence (within experimental limits) of two carbon resonances. The broadening or slight splitting in the resonances in both samples is possibly due to coupling of the  $^{13}\text{C}$  nuclei to  $^{103}\text{Rh}$  ( $S = 1/2$ , 100% abundance). We will discount  $\lambda$  and  $\delta$  conformational changes as the reason for peak splitting since resolution of conformations with such similar chemical shift would require a large activation energy between conformations [25]. Any free energy difference larger than 1 kcal/mol would lead to an equilibrium mixture containing  $\geq 85\%$  of the more stable conformer [24]. Since the split peaks are approximately the same intensity, it is far more reasonable to assume that splitting is occurring *via* spin-spin coupling.

A comparison of the chemical shifts of the series of *cis*- $\text{Rh}(\text{en})_2\text{XCl}^{n+}$  complexes (where  $\text{X} = \text{Cl}, \text{OH}_2, \text{NH}_3$ ) indicates that large chemical shift differences are observed when  $\text{X}$  is varied. The similar comparison for *trans*- $\text{Rh}(\text{en})_2\text{XCl}^{n+}$  complexes (when  $\text{X}$  and  $\text{Cl}$  are always *cis* to the ethylenediamine) indicates that the  $^{13}\text{C}$  chemical shifts are insensitive to  $\text{X}$ . The relatively small "cis effect" and relatively large "trans effect" can arise from a number of effects including both neighboring group anisotropy and electronic effects. The change in chemical shift as a function of neighboring group anisotropy is given by equation 1 [27]:

$$\Delta\sigma = \sum_i \frac{1 - 3 \cos^2\theta_i}{3R_i^3} (\chi_{\parallel} - \chi_{\perp})_i \quad i = \text{ligands} \quad (1)$$

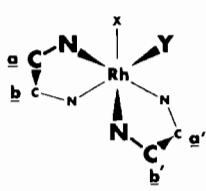
For the *trans* complexes the value of  $\theta$  between all four carbons and  $\text{X}$  lies between  $40^\circ$  and  $60^\circ$  and the geometric factor is small. The *cis* complexes have a variety of  $\theta$  values between the carbon atoms and  $\text{X}$  some of which lead to relatively large values of  $1 - 3 \cos^2\theta$ . Thus neighboring group anisotropy due to  $\text{X}$  can be very sensitive to the nature of  $\text{X}$  (if  $\Delta\chi$  is substantial), while changes in  $\text{X}$  do not substantially alter  $\sigma$  in the *trans* complexes due to the presence of a small geometric factor in equation 1. A similar result is obtained when electronic effects are considered. Changing  $\text{X}$  should cause the greatest changes in electronic distribution at the ligand *trans* rather than *cis* to  $\text{X}$  [28]. In the *trans* complexes, the *trans*-site is occupied by a  $\text{Cl}$  ligand while an ethylenediamine nitrogen occupies this site in the *cis* compounds. Therefore, we expect greater changes in electronic distribution around the carbon atoms (and therefore greater chemical shift differences) in the *cis* complexes.

The  $^{13}\text{C}$  chemical shift pattern, in the spectrum of *cis*- $\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}^{2+}$ , have enabled us to assign a *cis* configuration to the photolysis product of  $\text{Rh}(\text{en})_3^{3+}$  in an acidic, chloride solution. The primary photolysis product of  $\text{Rh}(\text{en})_3^{3+}$  ( $\lambda_{\text{irr}} = 313 \text{ nm}$ ,  $1 F \text{ HCl}$ ) is *cis*- $\text{Rh}(\text{en})_2(\text{enH})\text{Cl}^{3+}$  with secondary photolysis

leading to  $trans\text{-Rh(en)}_2\text{Cl}_2^+$  [29]. The C-13 nmr spectrum of the isolated photolysis mixture is shown in Figure 4. The presence of unreacted starting material ( $\text{Rh(en)}_3^{3+}$ ) and secondary photolysis product ( $trans\text{-Rh(en)}_2\text{Cl}_2^+$ ) have been confirmed by spiking the sample with the impurities. Computer subtraction techniques, using authentic spectra of  $\text{Rh(en)}_3^{3+}$  and  $trans\text{-Rh(en)}_2\text{Cl}_2^+$ , result in the spectrum shown in Figure 5. Figure 5 corresponds to a spectrum of pure  $cis\text{-Rh(en)}_2(\text{enH})\text{Cl}^{3+}$ . There is a close similarity to the spectrum of  $cis\text{-Rh(en)}_2(\text{NH}_3)\text{Cl}^{2+}$  (Fig. 3) and  $cis\text{-Rh(en)}_2(\text{enH})\text{Cl}^{3+}$  (Fig. 5). The chemical shifts (Table II) are 47.07, 46.27 and 45.81 (2 carbons) ppm for the former complex and 47.15, 46.56, 45.99 and 45.94 ppm for the latter complex. In addition, the spectrum of  $cis\text{-Rh(en)}_2(\text{enH})\text{Cl}^{3+}$  contains resonances at 43.30 and 40.59 (br) ppm due to the two carbons on the ethylenediaminium (enH) ligand. The most deshielded resonance (40.59 ppm) corresponds to the carbon  $\alpha$  to the  $\text{NH}_3^+$  end of the monodentate ligand. This resonance is deshielded with respect to the other signals due to polarization of the  $\alpha$ -carbon-nitrogen bond as a result of nitrogen protonation [30]. The broadening of this signal is also typical of carbon atoms which are  $\alpha$  to quarternary nitrogens [31]. There is no nmr evidence to indicate that any  $trans\text{-Rh(en)}_2(\text{enH})\text{Cl}^{3+}$  is formed in this photolysis reaction.

On the basis of the experimentally observed small "cis effects" and large "trans effects", we have tentatively assign the carbon resonances for all  $cis\text{-Rh(en)}_2\text{-XY}^{n+}$  complexes in Table III. In going from  $\text{Rh(en)}_3^{3+}$  (all carbons at 46.36 ppm) to  $cis\text{-Rh(en)}_2\text{Cl}_2^+$ , carbon atoms  $b$  and  $b'$  should be deshielded owing to the replacement of en by the two electronegative Cl ligands. Thus, we have assigned the 47.25 ppm resonance in  $cis\text{-Rh(en)}_2\text{Cl}_2^+$  to the  $b$  and  $b'$  carbon atoms (bound to nitrogen *trans* to Cl). The remainder of the series involves varying the X ligand in  $cis\text{-Rh(en)}_2\text{XCl}^{n+}$  complexes. The small "cis effect" observed for the  $trans\text{-Rh(en)}_2\text{XCl}^{n+}$  complexes, suggests that the  $a$  and  $b$  carbon atoms should be relatively insensitive to the changes in X. This leads to the assignments of 46.15, 45.98, 45.81 and 45.94 ppm for the  $a$  carbon atoms and 47.25, 47.07, 47.07 and 47.15 ppm for the  $b$  carbon atoms in  $cis\text{-Rh(en)}_2\text{XCl}^{n+}$  where X = Cl, OH<sub>2</sub>, NH<sub>3</sub>, and enH respectively. The largest differences in the series should be observed for the  $b'$  carbon atom which is directly bound to the nitrogen atom *trans* to the changing X group. We have tentatively assigned resonances at 47.25, 47.78, 45.81 and 45.99 ppm for the  $b'$  carbon atom when X = Cl, OH<sub>2</sub>, NH<sub>3</sub> and enH, respectively. The assignments for the  $a'$  carbon atoms are then 46.15, 45.20, 46.27 and 46.56 ppm, respectively, for X = Cl, OH<sub>2</sub>, NH<sub>3</sub> and enH. The  $cis\text{-Rh(en)}_2(\text{NH}_3)\text{Cl}^{2+}$  and  $cis\text{-Rh(en)}_2(\text{enH})\text{Cl}^{3+}$  complexes have their  $a'$  carbon atoms in an environment

TABLE III. Proposed <sup>13</sup>C Assignments for  $cis\text{-Rh(en)}_2\text{XY}^{n+}$  Complexes.



X	Y	a	a'	b	b'
en/2	en/2	46.36	46.36	46.36	46.36
Cl	Cl	46.15	46.15	47.25	47.25
OH <sub>2</sub>	Cl	45.98	45.20	47.07	47.78
NH <sub>3</sub>	Cl	45.81	46.27	47.07	45.81
enH <sup>1</sup>	Cl	45.94 <sup>2</sup>	46.56	47.15	45.99 <sup>2</sup>

<sup>1</sup> Assignments for the monodentate ethylenediaminium ligand correspond to 45.09 ppm for the carbon atom adjacent to the protonated nitrogen and 43.30 ppm for the carbon atom adjacent to the coordinated nitrogen (see text).

<sup>2</sup> The assignments of the  $a$  and  $b'$  carbons in this complex may be reverse owing to the difficulty in predicting the effect of the small difference in chemical environment.

that is electronically and magnetically similar to the carbon atoms in  $\text{Rh(en)}_3^{3+}$ . Our assignments place these carbon atoms at 46.27 and 46.56 ppm, respectively, in agreement with this observation ( $\text{Rh(en)}_3^{3+}$  at 46.36 ppm). Although these tentative assignments appear to be internally consistent and agree with simple chemical intuition, the limited knowledge concerning neighboring group anisotropic effects, electronic effects, and solvent effects, prevents the unequivocal assignment of the <sup>13</sup>C resonances.

There is one literature report involving <sup>13</sup>C spectra of  $\text{Rh(en)}_2\text{XY}^{n+}$  complexes where chemically non-equivalent carbon atoms do not show individual signals. Burgess and Hartley [9] have observed single <sup>13</sup>C resonances for both  $trans\text{-Rh(en)}_2\text{Br}_2^+$  (46.1 ppm) and  $cis\text{-Rh(en)}_2\text{Br}_2^+$  (46.9 ppm). The 46.1 ppm chemical shift of  $trans\text{-Rh(en)}_2\text{Br}_2^+$  is similar to the chemical shift observed for the other  $trans\text{-Rh(en)}_2\text{-XY}^{n+}$  in this study and is consistent with a small "cis effect". The presence of a single resonance for  $cis\text{-Rh(en)}_2\text{Br}_2^+$  [9] rather than the two observed in  $cis\text{-Rh(en)}_2\text{Cl}_2^+$  is puzzling. A possible explanation is that the two chemically non-equivalent pairs of carbon atoms in  $cis\text{-Rh(en)}_2\text{Br}_2^+$  are magnetically in coincidence. Further studies will be needed to confirm this hypothesis and also to establish unambiguous assignments for all of the carbon resonances.

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