

number of electrical carriers but these carriers do not appear to be free but rather close to the conduction band. In NiPS<sub>3</sub> the intercalation is more rapid and probably occurs as a two-phase phenomenon. The reduction in magnetic susceptibility as well as the large number of nonthermally activated electrons suggests the formation of a metallic intercalated phase. This argument is supported by recent NMR measurements which have observed a second phosphorus resonance peak with lithium intercalation.<sup>12</sup>

It is interesting to compare the results obtained by chemical intercalation with those previously reported for electrochemical discharge. For those materials which show no change in electrical conductivity with chemical intercalation the electrical discharge drops rapidly. NiPS<sub>3</sub> which is the material that chemically reacted the most rapidly and showed the largest change in electrical and magnetic properties has also shown the most favorable discharge curves. It must be emphasized that the chemical intercalations carried out with butyllithium were certainly not under thermodynamic equilibrium conditions and therefore would not necessarily yield the same results as those experiments made electrochemically.

**Registry No.** MnPSe<sub>3</sub>, 69447-58-1; FePSe<sub>3</sub>, 52226-00-3; FePS<sub>3</sub>, 42821-47-6; NiPS<sub>3</sub>, 42821-48-7; MnPS<sub>3</sub>, 43000-56-2; CdPS<sub>3</sub>, 60495-79-6; ZnPS<sub>3</sub>, 56172-70-4; LiMnPSe<sub>3</sub>, 70130-39-1; LiFePSe<sub>3</sub>, 70130-40-4; LiFePS<sub>3</sub>, 70130-41-5; LiNiPS<sub>3</sub>, 65756-46-9; *n*-butyllithium, 109-72-8.

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## Quantum Yields and Product Stereochemistry for the Photochemistry of *cis*- and *trans*-Rh(en)<sub>2</sub>XCl<sup>n+</sup> 1

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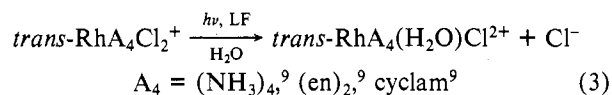
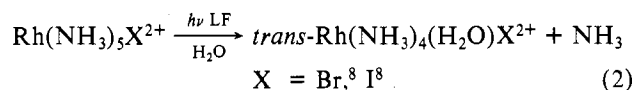
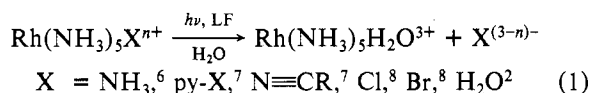
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The photoaquation quantum yields and product stereochemistries for *cis*- and *trans*-Rh(en)<sub>2</sub>XCl<sup>n+</sup> (X = Cl, NH<sub>3</sub>) are reported. All of the complexes undergo loss of chloro ligand and formation of Rh(en)<sub>2</sub>X(H<sub>2</sub>O)<sup>n+</sup> in aqueous solution. Photolysis of the *trans* complexes results in stereoretentive products with quantum yields of 0.061 and 0.062 mol/einstein for X = Cl and NH<sub>3</sub>, respectively. For the *cis* complexes, the stereochemistry of the product depends on the nature of X. For X = Cl, the quantum yield for chloro loss is 0.43 mol/einstein, and the product has a *trans* configuration. For X = NH<sub>3</sub>, chloro loss ( $\Phi = 0.145$  mol/einstein) results in the stereoretentive *cis* photoproduct. The stereochemical fate and mechanistic implications of the photolysis reactions of these Rh(III) amine complexes will be discussed in terms of existing theory.

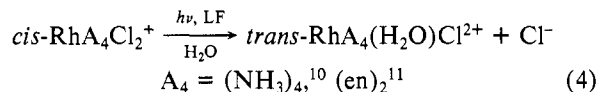
### Introduction

Ligand field photolysis of rhodium(III) amine complexes in aqueous solution customarily leads to the photoaquation of one ligand from the complex<sup>2</sup> resulting in a monoquo complex as the photolysis product. Subsequent ligand photosubstitution reactions are not observed spectroscopically since further reaction is usually limited to aquo ligand exchange.<sup>3</sup> Models<sup>4</sup> have been proposed to explain the nature of the labilized ligand although some ambiguities<sup>5</sup> arise in the correlation of theory to experiment.

Until recently, the theory on the photosubstitution reactions of rhodium(III) amine complexes has been limited to the nature of the labilized ligand with no effort spent on the stereochemistry of the remaining metal fragment. This apparent lack of study was manifested by the seemingly stereoretentive photochemical behavior of the Rh(III) complexes. Photolyses of pentaamminerhodium(III) systems (eq 1 and 2) and *trans*-disubstituted tetraamine complexes (eq 3) have



led solely to pentaammine or *trans*-disubstituted tetraamine photolysis products. It was not until studies on the photochemistry<sup>10,11</sup> of *cis*-dichlorotetraamminerhodium(III) complexes resulted in *trans* products (eq 4) did any thermal<sup>12</sup>



or photochemical substitution reaction of Rh(III) definitely indicate geometric isomerization around the metal center.

*Cis/trans* rearrangements of M(III) amine complexes are not limited to Rh(III). Both Co(III)<sup>13,14</sup> and Cr(III)<sup>15</sup> amine complexes display stereomobility during photosubstitution reactions. Vanquickenborne and Ceulemans<sup>16,17</sup> have been successful recently in using a ligand field treatment to explain the stereochemical changes around selected d<sup>3</sup> and d<sup>6</sup> metal centers.

In this work, we report the results of the ligand field photochemistry of some bis(ethylenediamine) complexes of Rh(III). In addition, we will use the ligand field analysis of Vanquickenborne and Ceulemans<sup>17</sup> to discuss the stereochemistry of the photolysis products of these reactions as well

Table I. Electronic Spectra of *cis*- and *trans*-[Rh(en)<sub>2</sub>XCl]<sup>n+</sup>

compd	$\lambda_{\max}$ , nm	$\epsilon_{\max}$ , M <sup>-1</sup> cm <sup>-1</sup>
<i>trans</i> -[Rh(en) <sub>2</sub> Cl <sub>2</sub> ]NO <sub>3</sub>	406	83 (75 <sup>a</sup> )
	286	134 (130 <sup>a</sup> )
<i>trans</i> -[Rh(en) <sub>2</sub> (NH <sub>3</sub> )Cl](NO <sub>3</sub> ) <sub>2</sub>	342	95 <sup>a</sup>
	275	120 <sup>a</sup>
<i>cis</i> -[Rh(en) <sub>2</sub> Cl <sub>2</sub> ]ClO <sub>4</sub>	352	203 <sup>b</sup>
	295	205 <sup>b</sup>
<i>cis</i> -[Rh(en) <sub>2</sub> (NH <sub>3</sub> )Cl](NO <sub>3</sub> ) <sub>2</sub>	342	150 <sup>a</sup>
	276	195 <sup>a</sup>

<sup>a</sup> Reference 9. <sup>b</sup> The NO<sub>3</sub><sup>-</sup> salt, which has 20% *trans* isomer as a contaminant, has  $\epsilon$  values of 155 and 180 M<sup>-1</sup> cm<sup>-1</sup>, respectively.

as photosubstitution reactions of other d<sup>6</sup> amine systems.

### Experimental Section

**Materials.** The recrystallized salts of *cis*- and *trans*-[Rh(en)<sub>2</sub>Cl<sub>2</sub>]NO<sub>3</sub> and *cis*- and *trans*-[Rh(en)<sub>2</sub>(NH<sub>3</sub>)Cl](NO<sub>3</sub>)<sub>2</sub> were prepared from the previously described procedures.<sup>18</sup> The purity of all of the above compounds was confirmed by electronic spectra<sup>18</sup> and by carbon-13 NMR spectroscopy.<sup>19</sup> The signal-to-noise ratio of the typical NMR spectra limited nondetectable geometric impurities to <5%. In all instances, except *cis*-[Rh(en)<sub>2</sub>Cl<sub>2</sub>]NO<sub>3</sub>, <sup>13</sup>C NMR confirmed the purity of the compounds. The *cis*-[Rh(en)<sub>2</sub>Cl<sub>2</sub>]NO<sub>3</sub> compound was found to contain 20% of the *trans* isomer, and purification required recrystallization as the perchlorate salt.<sup>19</sup>

Water used as the solvent for synthetic and photolytic reactions was redistilled from alkaline permanganate in an all-glass apparatus. All other reagents used in the preparation of the compounds were analytical reagents and were used without further purification.

**Apparatus.** Quantum yields were determined with a continuous-beam photolysis apparatus described elsewhere.<sup>20</sup> Usable intensities at the irradiation wavelengths of 405 and 365 nm were determined by ferrioxalate actinometry<sup>21</sup> and approximated 2.5 × 10<sup>18</sup> and 1.5 × 10<sup>18</sup> quanta/min, respectively.

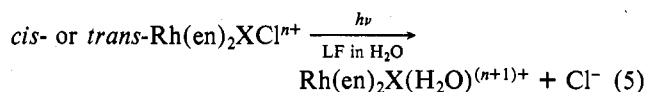
All absorption spectra and optical density measurements used to determine quantum yields were recorded on a Cary 14 spectrophotometer. The <sup>13</sup>C NMR spectra, which were used to check the purity of the reactants and confirm the geometric configuration of the photochemical products, were recorded on a Varian XL-100-15 spectrometer operating at a frequency of 25.2 MHz and equipped with a Nicolet FT-100 data system. NMR procedures and data treatment have been described previously.<sup>19,22</sup> A Corning Model 5 pH meter calibrated against commercially available buffer solutions was used to adjust the pH of the photolysis solutions.

**Photolysis Procedures.** All photolyses were carried out at 25 °C in 0.014 M HClO<sub>4</sub> in 2-cm, cylindrical, quartz cells. Quantum yields were calculated from changes in the electronic spectra as a function of irradiation time. Photolysis products were identified by <sup>13</sup>C NMR with the product extinction coefficient values obtained from independent synthesis. All photolysis reactions gave isosbestic points to >50% reaction; however, the quantum yields reported in this work are initial quantum yields obtained by extrapolation to 0% reaction by previously reported procedures.<sup>20</sup> No thermal reactions of the reactants or products were detected during the time scale of the photolysis experiments.

### Results

The electronic absorption spectra of the *cis*- and *trans*-Rh(en)<sub>2</sub>XCl<sup>n+</sup> complexes studied in this work appear in Table I. These spectra are dominated by two ligand field absorption

bands (derived from <sup>1</sup>T<sub>1</sub> ← <sup>1</sup>A<sub>1</sub> and <sup>1</sup>T<sub>2</sub> ← <sup>1</sup>A<sub>1</sub> in the octahedral point group). Irradiation in aqueous solution of the lowest ligand field band of each complex (Table II) leads to photoaquation of a chloro ligand (eq 5).



For the *trans*-Rh(en)<sub>2</sub>XCl<sup>n+</sup> complexes, where X = Cl or NH<sub>3</sub>, the photoaquation reaction is stereoretentive, resulting in *trans*-Rh(en)<sub>2</sub>Cl(H<sub>2</sub>O)<sup>2+</sup> and *trans*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)(H<sub>2</sub>O)<sup>3+</sup>, respectively, as the primary photolysis products. The photoaquation quantum yield for *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> that we report in Table II (0.061 mol/einstein at  $\lambda_{\text{irr}}$  405 nm) is virtually identical to the value reported by Kutal and Adamson<sup>9</sup> (0.057 mol/einstein at  $\lambda_{\text{irr}}$  407 nm). Irradiation of the *trans*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)Cl<sup>2+</sup> complex ion at 365 nm resulted in the formation of *trans*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)(H<sub>2</sub>O)<sup>3+</sup> with a quantum yield virtually identical to that of the dichloro complex ( $\Phi_{\text{Cl}} = 0.062$  mol/einstein). The *trans* configuration of both photochemical products discussed above has been confirmed by electronic and <sup>13</sup>C magnetic resonance spectroscopy.

The results of the photolysis of the *cis*-Rh(en)<sub>2</sub>XCl<sup>n+</sup> isomers are drastically different from those of the *trans* counterparts described above. The photochemical product is still the Rh(en)<sub>2</sub>X(H<sub>2</sub>O)<sup>n+</sup> species, but the stereochemistry of the product is dependent on the nature of X. For X = Cl, the quantum yield for chloro ligand loss is 0.43 mol/einstein ( $\lambda_{\text{irr}}$  365 nm), but the product is exclusively the *trans* isomer, *trans*-Rh(en)<sub>2</sub>Cl(H<sub>2</sub>O)<sup>2+</sup>.<sup>23</sup> The 100% stereoisomerization observed for this photochemical reaction has been confirmed by <sup>13</sup>C NMR studies.<sup>19</sup> Muir and Huang<sup>11a</sup> have estimated the total quantum yield for isomerization of *cis*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> at 0.38 mol/einstein ( $\lambda_{\text{irr}}$  350 nm) which is consistent with our results. However, these researchers<sup>11a</sup> also detected some *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> in the photolysis product which has since been attributed<sup>19</sup> to the presence of 20–25% of the *trans* isomer in *cis*-[Rh(en)<sub>2</sub>Cl<sub>2</sub>]NO<sub>3</sub> prepared by the standard literature procedure.<sup>18</sup>

In contrast to the *cis*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> system, the ligand field photolysis of *cis*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)Cl<sup>2+</sup> leads to ≥90% *cis* products as determined by <sup>13</sup>C NMR spectroscopy. The photolysis product, *cis*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)(H<sub>2</sub>O)<sup>3+</sup>, is formed with a quantum yield of 0.145 mol/einstein at  $\lambda_{\text{irr}}$  365 nm (Table II).

### Discussion

The photoaquation of the *trans*-Rh(en)<sub>2</sub>XCl<sup>n+</sup> complexes (X = Cl, NH<sub>3</sub>) proceeds in a stereoretentive fashion resulting in *trans*-Rh(en)<sub>2</sub>X(H<sub>2</sub>O)<sup>n+</sup> as the sole photolysis product. The similarities in the two quantum yields ( $\Phi_{\text{Cl}} = 0.061$  mol/einstein for X = Cl;  $\Phi_{\text{Cl}} = 0.062$  mol/einstein for X = NH<sub>3</sub>) is certainly coincidental since the two systems require removing a chloro ligand from complexes of different charges, different energies of the lowest excited state, and most probably different excited-state lifetimes; however, the same coincidental behavior is observed when (en)<sub>2</sub> is replaced by (NH<sub>3</sub>)<sub>4</sub> to give *trans*-Rh(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> ( $\Phi_{\text{Cl}} = 0.13$  mol/einstein<sup>9</sup>) and Rh(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> ( $\Phi_{\text{Cl}} = 0.14$  mol/einstein<sup>8</sup>).

Table II. Quantum Yields for the Photoaquation of Cl<sup>-</sup> from Rh(en)<sub>2</sub>XCl<sup>n+</sup>

compd	$\lambda_{\max}$ , nm <sup>a</sup>	$\lambda_{\text{irr}}$ , nm	$\Phi_{\text{Cl}}^b$	photoproduct
<i>trans</i> -Rh(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	406	405	0.061 ± 0.003 (4)	<i>trans</i> -Rh(en) <sub>2</sub> (H <sub>2</sub> O)Cl <sup>2+</sup>
		407 <sup>c</sup>	0.057 ± 0.002 <sup>c</sup>	
<i>trans</i> -Rh(en) <sub>2</sub> (NH <sub>3</sub> )Cl <sup>2+</sup>	342	365	0.062 ± 0.001 (6)	<i>trans</i> -Rh(en) <sub>2</sub> (NH <sub>3</sub> )(H <sub>2</sub> O) <sup>3+</sup>
<i>cis</i> -Rh(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	352	365	0.43 ± 0.02 (4)	<i>trans</i> -Rh(en) <sub>2</sub> (H <sub>2</sub> O)Cl <sup>2+</sup>
<i>cis</i> -Rh(en) <sub>2</sub> (NH <sub>3</sub> )Cl <sup>2+</sup>	342	365	0.145 ± 0.006 (4)	<i>cis</i> -Rh(en) <sub>2</sub> (NH <sub>3</sub> )(H <sub>2</sub> O) <sup>3+</sup>

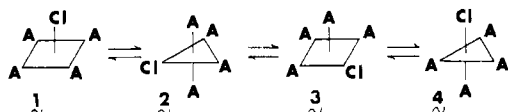
<sup>a</sup> Maximum in nm of lowest energy, singlet, ligand field transition derived from <sup>1</sup>T<sub>1</sub> ← <sup>1</sup>A<sub>1</sub> in the octahedral ligand field. <sup>b</sup> Quantum yield for loss of chloride; reported in units of mol/einstein with the appropriate average deviation and the number of independent determinations in parentheses. <sup>c</sup> Reference 9.

The photochemistry of the cis isomers, *cis*-Rh(en)<sub>2</sub>XCl<sup>m+</sup> (X = Cl, NH<sub>3</sub>), is not as straightforward as the trans isomers. The primary photochemical product has the same formula as the trans systems, Rh(en)<sub>2</sub>X(H<sub>2</sub>O)<sup>m+</sup>, but the stereochemistry of the photolysis product is dependent on the nature of X. When X = NH<sub>3</sub>, photoaquation is stereoretentive ( $\Phi_{\text{Cl}} = 0.145$  mol/einstein) while the X = Cl complex results in 100% stereoconversion to the trans isomer ( $\Phi_{\text{Cl}} = 0.43$  mol/einstein). There are three different mechanisms that have been proposed for the photoisomerization/photoaquation of *cis*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> and homologous Co(III) systems. (1) The primary photochemical reaction is loss of Cl<sup>-</sup> leading to an intermediate which stereospecifically adds H<sub>2</sub>O to the complex in a position trans to the remaining Cl<sup>-</sup>.<sup>1a,10</sup> (2) The primary photochemical step may be cis to trans isomerization of Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> followed by the secondary photolysis of *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>.<sup>11</sup> (3) The primary photochemical step is labilization of one end of an ethylenediamine (trans to Cl) followed by displacement of a chloro ligand by the uncoordinated amine.<sup>11a,13b</sup>

Mechanism (2) cannot be viable since the production of *trans*-Rh(en)<sub>2</sub>(H<sub>2</sub>O)Cl<sup>2+</sup> occurs by a process which has a greater quantum yield than that obtained from direct irradiation of the trans dichloro complex. Also, isosbestic points throughout the reaction indicated that no secondary photochemical reaction is occurring. Mechanism (3) appears unlikely because of two results. Strauss and Ford<sup>10</sup> find that ligand field irradiation of *cis*-Rh(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> leads solely to *trans*-Rh(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl<sup>2+</sup> as the photolysis product, which in the absence of chelating amine ligands indicates that the primary photochemical process is cleavage of the Rh-Cl bond. We have also found<sup>24</sup> that irradiation of Rh(en)<sub>3</sub><sup>3+</sup> in chloride media leads to a photolysis product in which monodentate ethylenediamine and chloro ligands exist in a stable compound in adjacent coordination sites. Therefore, we feel that mechanism (1) best describes the photochemistry of *cis*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>.

The fact that the photoaquation of chloride from *cis*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> and *cis*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)Cl<sup>2+</sup> results in products with different stereochemistry indicates that there is a coordination-sphere influence on the site of attack by incoming aquo ligand. Although an associative mechanism for d<sup>6</sup> photo-substitution reactions has not been ruled out, the experimental evidence<sup>2,9,11</sup> as well as theoretical treatments<sup>4</sup> have pointed to a simple dissociative initial step.

The photochemistry and product stereochemistry of *cis*- and *trans*-Rh(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> parallel those of analogous *cis*-<sup>10</sup> and *trans*-<sup>9</sup>-Rh(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>. In general, photolysis of *cis*- or *trans*-RhA<sub>4</sub>Cl<sub>2</sub><sup>+</sup> (A<sub>4</sub> = (NH<sub>3</sub>)<sub>4</sub> or (en)<sub>2</sub>) leads to *trans*-RhA<sub>4</sub>(H<sub>2</sub>O)Cl<sup>2+</sup> photolysis products. Vanquickenborne and Ceulemans<sup>17</sup> have proposed, from calculations using an additive-point ligand field model, that stereomobility is occurring from a triplet, five-coordinate fragment. In the case of Rh(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>, the intermediates and their pathway of interconversion are shown as 1-4. Photochemically, 1 and 3

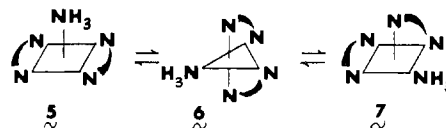


are formed directly from loss of Cl<sup>-</sup> from *trans*- and *cis*-Rh(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>, respectively. From Vanquickenborne and Ceulemans' calculations, the lowest energy triplet fragment is 1 which is separated from another minimum at 3 by a barrier of 0.28 μm<sup>-1</sup> at 2. The barrier in going from 3 to 2 is only ~0.11 μm<sup>-1</sup> while that from 3 to 4 is a very steeply increasing potential energy surface and therefore inaccessible.

The interpretation<sup>17</sup> of the photochemistry of the tetraammine complexes should also apply to the spectroscopically similar bis(ethylenediamine) system. For A = 1/2 en, structure

4 does not apply since it requires one of the bidentate en ligands to span 120°. When 1 is formed from the loss of Cl<sup>-</sup> from *trans*-RhA<sub>4</sub>Cl<sub>2</sub><sup>+</sup> (A<sub>4</sub> = (NH<sub>3</sub>)<sub>4</sub> or (en)<sub>2</sub>), the large barrier at 2 prevents racemization to 3. As a result, the triplet, square-pyramidal complex undergoes intersystem crossing to the singlet, ground-state, square-pyramidal complex, and adds a solvent molecule to give *trans*-RhA<sub>4</sub>Cl(H<sub>2</sub>O)<sup>2+</sup>. Formation of the triplet, five-coordinate fragment 3 from loss of Cl<sup>-</sup> from *cis*-RhA<sub>4</sub>Cl<sub>2</sub><sup>+</sup> (A<sub>4</sub> = (NH<sub>3</sub>)<sub>4</sub> or (en)<sub>2</sub>) follows a different pathway. In going from 3 to 1, there is a much smaller barrier at 2 than for the reverse rearrangement, so that interconversion of 3 to 1 is a viable process during the lifetime of the triplet, five-coordinate, excited-state fragment. Since the reverse process (1 to 3) does not occur, intermediate 1 acts as a trap and results solely in *trans*-RhA<sub>4</sub>Cl(H<sub>2</sub>O)<sup>2+</sup> as the photolysis product for both cis and trans starting materials.

The stereochemistry associated with the photoaquation of *cis*- and *trans*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)Cl<sup>2+</sup> is different from that observed for the dichloro complex. Both chloroammine isomers undergo chloro-ligand photoaquation, but unlike the case of the dichloro analogue, stereochemical retention is observed for both isomers. The structures of interest in determining the stereochemistry of the product are 5-7. Photochemically, 5



and 7 are formed directly from loss of Cl<sup>-</sup> from *trans*- and *cis*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)Cl<sup>2+</sup>, respectively. Since the σ- and π-bonding abilities of ammonia and ethylenediamine are similar, there should not be an energetic preference between 5 and 7. If the barrier from 5 to 6 is accessible within the lifetime of the triplet, five-coordinate fragment,<sup>17</sup> both *cis*- and *trans*-chloroammine starting materials should result in ~50% each of *cis*- and *trans*-aquoammine photolysis products. Since this is not the case, and only stereoretentive photoaquation is observed in both cases, the barrier between 5 and 7 must be too large to allow conversion of geometry.

The results of experimental as well as theoretical<sup>17</sup> work indicate that there is a definite tendency for photochemical intermediates of the type RhA<sub>4</sub>Cl<sup>2+</sup> (A<sub>4</sub> = (NH<sub>3</sub>)<sub>4</sub> or (en)<sub>2</sub>) to produce trans products. A cursory view<sup>25</sup> of the intermediate fragments by using an angular-overlap approach suggests that this preference is general whenever X is a weaker σ bond than A. This geometric preference does appear to be general for other weak σ-bonding systems as the same geometric product distributions are observed<sup>26</sup> for the photolysis of *cis*- and *trans*-Rh(en)<sub>2</sub>Br<sub>2</sub><sup>+</sup> and *cis*- and *trans*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)Br<sup>2+</sup>. These results also indicate that previous data<sup>8</sup> on the photolysis of Rh(NH<sub>3</sub>)<sub>5</sub>X<sup>2+</sup> (X = Br, I) may need further study. The major photolysis product, *trans*-Rh(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)X<sup>2+</sup>, now appears likely regardless of whether a cis or trans ammonia ligand is lost during irradiation.

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**Registry No.** *trans*-[Rh(en)<sub>2</sub>Cl<sub>2</sub>]NO<sub>3</sub>, 34768-40-6; *trans*-[Rh(en)<sub>2</sub>(NH<sub>3</sub>)Cl](NO<sub>3</sub>)<sub>2</sub>, 65802-28-0; *cis*-[Rh(en)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>, 67047-30-7; *cis*-[Rh(en)<sub>2</sub>(NH<sub>3</sub>)Cl](NO<sub>3</sub>)<sub>2</sub>, 70178-70-0; *trans*-Rh(en)<sub>2</sub>(H<sub>2</sub>O)Cl<sup>2+</sup>, 15337-41-4; *trans*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)(H<sub>2</sub>O)<sup>3+</sup>, 15337-82-3; *cis*-Rh(en)<sub>2</sub>(NH<sub>3</sub>)(H<sub>2</sub>O)<sup>3+</sup>, 70223-45-9.

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## [Rh<sub>17</sub>(S)<sub>2</sub>(CO)<sub>32</sub>]<sup>3-</sup>. 2. <sup>13</sup>C NMR Variable-Temperature Study of a Cluster with Localized Carbonyl Fluxionality

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The <sup>13</sup>C NMR behavior of the benzyltriethylammonium salt of [Rh<sub>17</sub>(S)<sub>2</sub>(CO)<sub>32</sub>]<sup>3-</sup> has been studied. The anion could be enriched at 125 °C with no evidence for preferential carbonyl exchange. The limiting, slow-exchange spectrum observed at 40 °C indicates that the solid-state structure is also present in solution. Carbonyl scrambling appears at 60 °C, and coalescence is observed at 120 °C with an estimated free energy of activation of 17.2 ± 0.4 kcal/mol. The unchanged appearance of the resonances at 252.7 and 194.1 ppm and the simultaneous thermal variation of the resonances at 231.3 and 196.8 ppm are interpreted as evidence for the rigid and fluxional characters, respectively, of the two sets of bridging and terminal carbonyl ligands. A full assignment of these resonances is suggested and a mechanism is proposed for the carbonyl scrambling.

### Introduction

The high chemical stability of [Rh<sub>17</sub>(S)<sub>2</sub>(CO)<sub>32</sub>]<sup>3-</sup> and the novelty of the structure<sup>1,2</sup> induced us to investigate its behavior in solution, via <sup>13</sup>C variable-temperature NMR spectroscopy. A main purpose of these studies was to gather information about the fluxional properties of the carbonyl ligands that would lead to the completion of previous assignments.<sup>1,2</sup> Moreover, the unusual stability of this cluster and its relative chemical inertness under a variety of reaction conditions<sup>1,2</sup> offered the opportunity for testing of the suggested relationship between fluxionality and reactivity of polynuclear rhodium carbonyl complexes.<sup>3</sup>

We have previously reported the <sup>13</sup>C NMR spectrum of [Rh<sub>17</sub>(S)<sub>2</sub>(CO)<sub>32</sub>]<sup>3-</sup> at 40 °C, with the conclusion that the solid-state structure of the anion is also present in solution.<sup>1,2</sup> We present additional evidence in this report relating to the fluxionality of the carbonyl ligands in the range of -40 to +180 °C together with a probable explanation for the peculiar fluxional behavior of the carbonyl groups of this cluster.

### Experimental Section

The salt [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub>[Rh<sub>17</sub>(S)<sub>2</sub>(CO)<sub>32</sub>], was prepared as previously described.<sup>2</sup> Solutions in acetone-*d*<sub>6</sub> or sulfolane-*d*<sub>6</sub> (tetrahydrothiophene 1,1-dioxide) were prepared by dissolving 0.42 g (0.127 mmol) and 0.85 g (0.259 mmol) of the compound in 3 mL of these solvents, respectively, and adding in both cases ca. 20 mg of Cr(acac)<sub>3</sub> as a relaxation agent. The former solution was studied in the range of -60 to +40 °C and the latter from 40 up to 180 °C.

The enrichment experiments were conducted by stirring the sulfolane-*d*<sub>6</sub> solution under 1 atm of <sup>13</sup>CO, 90% enriched, at 40 °C and 125 °C for 72 and 168 h, respectively.

Spectra were recorded on a Varian XL-100 NMR spectrometer equipped with Fourier transform capabilities using 12-mm sample tubes. A hertz per point value of 0.46 has been used during the whole study. The spectra of the nonenriched sample were obtained by accumulation of 20 000 transients with a 20 μs pulse width and an acquisition time of 1.0 s. Only 2000 transients were collected with the enriched sample, with the same pulse width and acquisition time as those above. Chemical shifts are reported in ppm downfield from tetramethylsilane, used as an external standard.

### Results and Discussion

Spectra obtained with a sample treated with enriched <sup>13</sup>CO at 40 °C for 72 h showed no significant difference from those of the nonenriched sample. By contrast, a sample warmed to 125 °C for 168 h under the same gaseous phase gave spectra consistent with <sup>13</sup>CO enrichment at all the CO sites of the cluster. The absence of <sup>13</sup>C-<sup>13</sup>C coupling has been taken as an indication that enrichment has occurred to an extent of 20-30% or less. The similarity between the spectra shown by both the nonenriched<sup>1,2</sup> and the enriched samples (Figure 1) indicates the absence of preferential exchange of the carbonyl ligands under these conditions.

The variation of the spectra with temperature (Figure 1) shows that the low-temperature limiting spectrum is observed at 40 °C, with changes in line width resulting at lower temperatures. Changes in the spectra start appearing at 60