

Identification of the Products of Photolysis Reactions of *cis*- and *trans*-Amminechloro- and Ammineaquabis(1,2-ethanediamine)-rhodium(III) Complexes by ^{13}C NMR Spectroscopy

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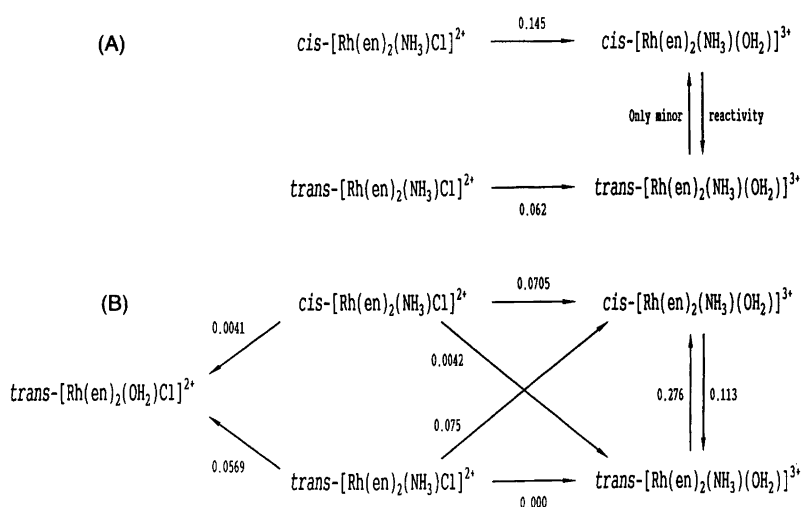
The *cis*- and *trans*-amminechlorobis(1,2-ethanediamine)rhodium(III) ions have been irradiated at 366 nm and 25 °C, and the photolysis products identified by ^{13}C NMR spectroscopy. Both complexes lose the chloride ligand on irradiation, and both form the *cis*-ammineaquabis(1,2-ethanediamine) complex as the primary product. The *trans*-amminechloro complex also loses ammonia during irradiation and forms the *trans*-aquaachlorobis(1,2-ethanediamine)rhodium(III) ion. This complex is only a minor product on irradiation of the *cis*-amminechloro complex. The *cis*- and *trans*-ammineaquabis(1,2-ethanediamine)rhodium(III) ions isomerize to a photostationary state containing comparable concentrations of the two complexes when irradiated at 366 nm.

The photochemical reactivity of the isomeric ammineaquabis(1,2-ethanediamine)rhodium(III) and amminechlorobis(1,2-ethanediamine)rhodium(III) ions was first investigated by a combination of ^{13}C NMR spectroscopy for product identification and UV–VIS spectrophotometry for quantum yield determination.^{1,2} The results of this work can be summarized as a stereoretentive chloride ligand photoaquation, followed by a strongly temperature-dependent photoisomerization between the generated ammineaquabis(1,2-ethanediamine)rhodium(III) isomers.

A recent reinvestigation of this system supplemented with photochemical water ligand exchange studies and photoracemization studies³ was not in agreement with

these previous results. Instead *cis*-ammineaquabis(1,2-ethanediamine)rhodium(III) was found to be the dominant product of photolysis of both amminechlorobis(1,2-ethanediamine)rhodium(III) isomers. Significant photochemical ammine ligand aquation was also found to occur, particularly in the *trans* complex, and at 25 °C photoisomerization of the ammineaquabis(1,2-ethanediamine)rhodium(III) isomers was found to take place with fairly large quantum yields. In this study the reactions were followed spectrophotometrically, and the products and quantum yields were determined by a multiwavelength analysis of the spectrophotometric data.

The significant discrepancy between these studies is



Scheme 1. Summary of the results published for the photochemical reactions of *cis*- and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ irradiated at 366 nm and 25 °C, (A) Refs. 1 and 2; (B) Ref. 3.

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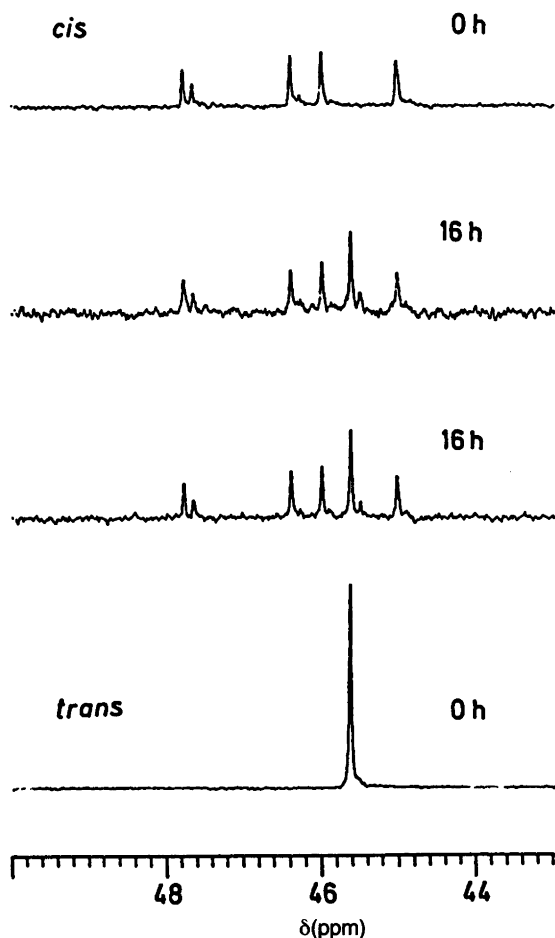


Fig. 1. Proton decoupled ^{13}C NMR spectra of *cis*- and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ before irradiation and after 16 h irradiation, respectively. The chemical shifts are given in Table 1. The splitting always seen for the resonance at 47.79 ppm of the *cis* complex is caused by slow exchange of hydrogen atoms by deuterium on the amine nitrogens. When the solutions are aged all resonances will split analogously for all the complexes. The nitrogen atom of the *cis* complex which exchanges hydrogen substantially faster than the other nitrogen atoms is probably the nitrogen in a *trans* position to water.

shown in Scheme 1. The differences can hardly be the result of a change of reaction medium from 0.014 M HClO_4 ^{1,2} to 0.5 M HClO_4 + 0.5 M NaClO_4 ,³ and it was therefore decided to reinvestigate the system by ^{13}C NMR spectroscopy.

Results and discussion

Solutions of *cis*- and *trans*-ammineaqua- and amminechlorobis(1,2-ethanediamine)rhodium(III) complexes were irradiated at 366 nm in acidic aqueous solutions, and the photochemical reactions followed by ^{13}C NMR as a function of time. The reactions of these four individual complexes will be treated separately, as described below:

cis- and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$. In Fig. 1 are shown the proton decoupled ^{13}C NMR spectra of *cis*- and *trans*-[Rh

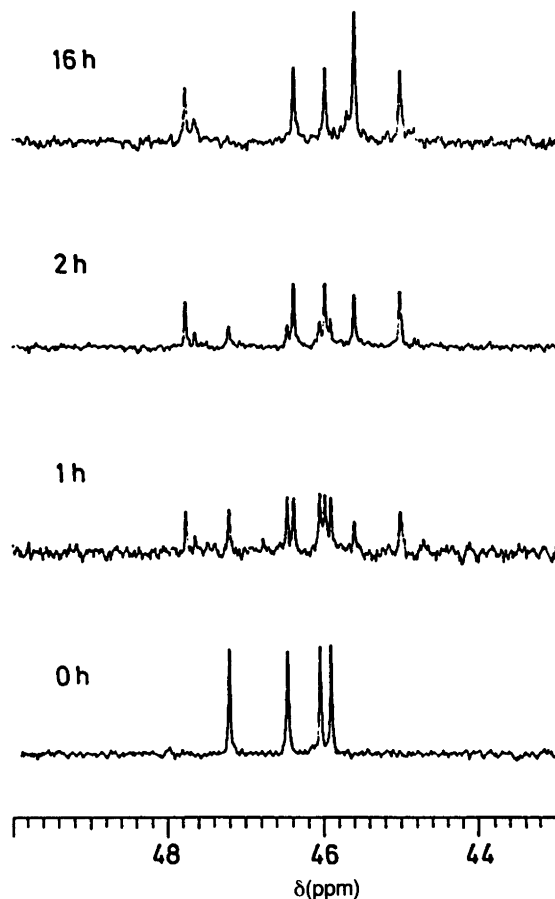


Fig. 2. Proton decoupled ^{13}C NMR spectra of *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ as a function of irradiation time. Chemical shifts are given in Table 1.

$(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ ions before and after irradiation for 16 h at 366 nm and 25 °C. The spectra of the non-irradiated solutions show one resonance for the *trans* compound and four resonances for the *cis* compound, as expected, and within the detection limits of the NMR spectrometer the compounds are seen to be pure. Solutions of the two isomers after irradiation for 16 h are seen to have identical spectra, indicating that a photostationary mixture has been formed. The ratio between the concentrations of the *trans* and the *cis* isomers is about 0.6 judged from the integrals. This is in excellent agreement with predictions based on the results given in Ref. 3 and presented in Scheme 1B.

It is contrary, however, to the results in Ref. 2, where it has been reported that only irradiation of these isomers at 50 °C leads to significant photoisomerization, and that irradiation at 25 °C is accompanied by only minor photoreactivity. This was explained by an energy barrier between an apical and a basal five-coordinated intermediate large enough to prevent isomerization at the lower temperature.

However, attempts to reproduce this temperature dependence were not successful, and irradiation of the *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ complex at 50 °C gave exactly the same results as the experiment at 25 °C, except for a split-

ting of all the ^{13}C resonances caused by thermal exchange of hydrogen for deuterium on the amine nitrogens (see the legend to Fig. 1).

cis- and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$. The molar absorption coefficients of the *cis-* and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ complexes are rather small compared to the molar absorption coefficients of the *cis-* and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ complexes at 366 nm. Therefore, this wavelength provides the best possibility for detection of the primary photopro-

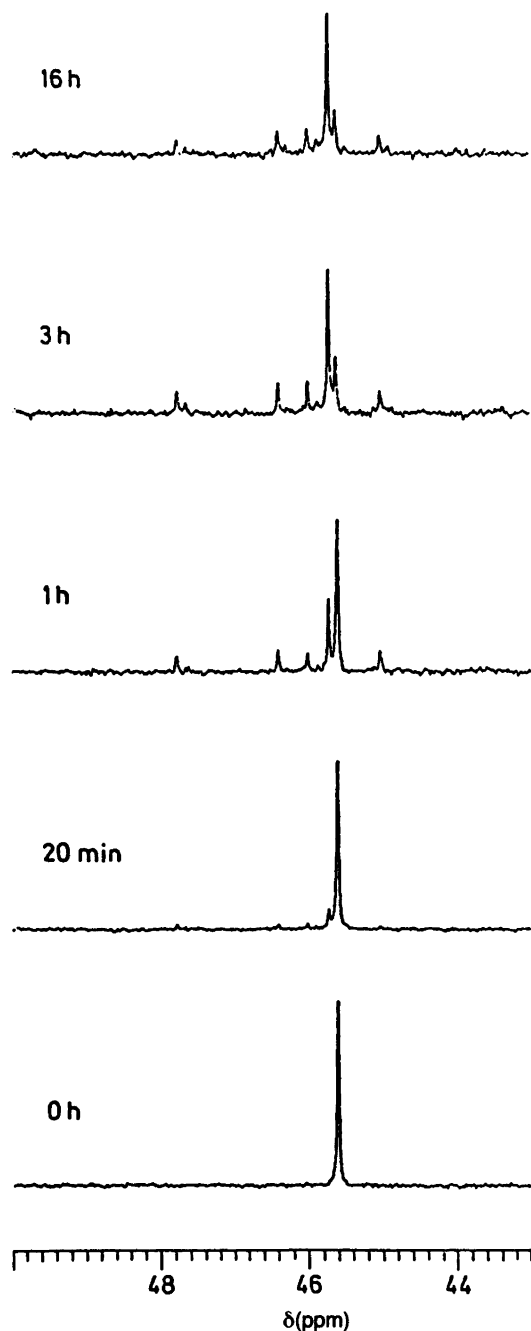


Fig. 3. Proton decoupled ^{13}C NMR spectra of *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ as a function of irradiation time. Chemical shifts are given in Table 1.

ducts which at lower wavelengths readily photoisomerize. In Fig. 2 is shown the proton decoupled ^{13}C NMR spectra of *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ as a function of the irradiation time. The spectrum of the non-irradiated solution shows four resonances as expected, and there are no signs of impurities. The spectra after irradiation for 1 and 2 h, respectively, show that both *cis-* and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ are formed during the reaction. After irradiation for 1 h the *trans/cis* concentration ratio is about 0.15, whereas the ratio after 2 h of irradiation is about 0.25. This indicates that the *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ complex is the dominant primary photoproduct, which then isomerizes to give the *trans* isomer. In agreement with this, the spectrum after 16 h of irradiation is identical with the spectrum of the exhaustively photolysed aqua complexes (Fig. 1) except for the small resonance at 45.59 ppm. This is attributed to the formation of *trans*- $[\text{Rh}(\text{en})_2(\text{OH}_2)\text{Cl}]^{2+}$ as predicted from the quantum yields of Scheme 1.

In Fig. 3 is shown the proton decoupled ^{13}C NMR spectra of irradiated *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ as a function of irradiation time. The spectrum of the non-irradiated solution confirms the purity of the compound, but after irradiation for 20 min an additional resonance from the *trans*- $[\text{Rh}(\text{en})_2(\text{OH}_2)\text{Cl}]^{2+}$ complex is clearly seen, and it is also just possible to detect the 4 resonances from *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$. After 1 and 3 h of irradiation, respectively, these resonances are more pronounced. It is not possible, with the spectrometer used, to resolve adequately the resonances from *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$. The ^{13}C NMR spectrum of a solution containing equal amounts of *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ shows two closely overlapping resonances with an overall linewidth for the two resonances of ca. 2.5 Hz, and with the resonances only just resolved when a line broadening of 1 Hz is added to improve signal-to-noise ratio to a satisfactory level. Therefore, for mixtures containing only small amounts of one of these complexes, it is not possible to determine the amounts of the minor species from our ^{13}C NMR spectra. Nevertheless, we observe that the chemical shift of one of the resonances changes from 45.59 to 45.62 ppm (Table 1) as a function of irradiation time. This indicates that the *trans*-chloroamine complex disappears and that the *trans*-ammineaqua complex is formed. The merged resonances for these two complexes have a chemical shift of 45.59 ppm after 1 h of irradiation, which is identical to that of the pure *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ complex. The concentration of the *trans*-ammineaqua complex is therefore much smaller than the concentration of the parent *trans*-amminechloro complex, and since a considerable amount of the *cis*-ammineaqua complex has been formed at this stage of the photolysis, this is independent evidence that the dominant primary photoproduct in the photochemical loss of a chloride ligand from the *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ complex is *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$. After irradiation for 16 h the spectrum shows a relatively large resonance from *trans*- $[\text{Rh}(\text{en})_2(\text{OH}_2)\text{Cl}]^{2+}$, in addition to the spectral characteristics

Table 1. ^{13}C chemical shifts for the non-irradiated solutions and for *cis*- and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ after irradiation for 1 and 16 h, respectively.^{a,b} (See also Scheme 1 and Figs. 1 and 2.)

| Complex irradiated | Chemical shifts (ppm) | | | | | | | | | | |
|--|-----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 0 h | | | | | | | | | | | |
| <i>trans</i> - $[\text{Rh}(\text{en})_2(\text{OH}_2)\text{Cl}]^{2+}$ | — | — | — | — | — | — | — | 45.73 | — | — | — |
| <i>trans</i> - $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ | — | — | — | — | — | — | — | — | — | 45.59 | — |
| <i>trans</i> - $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ | — | — | — | — | — | — | — | — | 45.64 | — | — |
| <i>cis</i> - $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ | — | 47.22 | 46.47 | — | 46.06 | — | 45.92 | — | — | — | — |
| <i>cis</i> - $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ | 47.79 | — | — | 46.40 | — | 46.00 | — | — | — | — | 45.04 |
| 1 h | | | | | | | | | | | |
| <i>trans</i> - $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ | 47.77 | — | — | 46.39 | — | 45.99 | — | 45.71 | — | 45.59 | 45.03 |
| <i>cis</i> - $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ | 47.78 | 47.22 | 46.47 | 46.39 | 46.06 | 45.99 | 45.92 | — | 45.62 | — | 45.03 |
| 16 h | | | | | | | | | | | |
| <i>trans</i> - $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ | 47.78 | — | — | 46.39 | — | 46.00 | — | 45.72 | 45.63 | — | 45.03 |
| <i>cis</i> - $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ | 47.78 | — | — | 46.39 | — | 45.99 | — | 45.72 | 45.62 | — | 45.03 |

^aThe values are in agreement with the values given in Refs. 1 and 4. ^bChemical shifts are reported vs. Me_4Si with dioxane (67.4 ppm) as an internal reference.

of the expected photostationary mixture of *cis*- and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$.

The ^{13}C NMR spectra have so far substantiated the photochemistry reported in Ref. 3, and as shown in Fig. 4 there is also a good agreement between the concentrations of *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ found from integration of the ^{13}C NMR spectra and the concentrations calculated from the quantum yields, molar absorption coefficients and the reaction scheme given in Ref. 3 (Scheme 1B).

Conclusions

This work has shown that the photochemical reaction scheme and quantum yields outlined in Scheme 1B (Ref. 3)

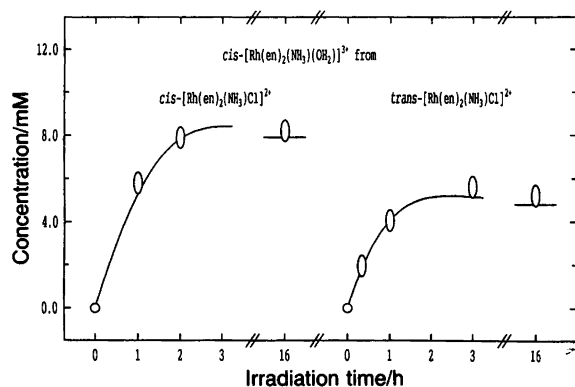


Fig. 4. Concentrations of *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ as a function of irradiation time for the photochemical reactions of *cis*- and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$, respectively. The points are experimental values found from integration of the ^{13}C NMR spectra drawn with a vertical extent corresponding to \pm the estimated uncertainty, and the curves are calculated from the quantum yields, molar absorption coefficients and the reaction scheme published in Ref. 3 (Scheme 1B).

are correct within the given error limits, and that monitoring photochemical transformations by UV-VIS spectrophotometry is a reliable method, particularly when the data are treated rigorously by the multiwavelength calculations described earlier.⁵ In the present case UV-VIS spectrophotometry is even more informative than ^{13}C NMR spectroscopy because, using the present spectrometer, it is impossible to separate adequately resonances as close as 0.03 ppm from the *trans*- $[\text{Rh}(\text{en})_2(\text{OH}_2)\text{Cl}]^{2+}$ and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ ions.

Experimental

Chemicals. *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}](\text{NO}_3)_2$, *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}](\text{CF}_3\text{SO}_3)_2$, *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{NO}_3)](\text{ClO}_4)_2$ and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)](\text{ClO}_4)_3$ were prepared by literature methods.³ Most of the compounds used were the same as were used for the investigation in Ref. 3. D_2O was from the Cambridge Isotope Laboratories. HClO_4 was of analytical grade.

NMR measurements. The proton decoupled ^{13}C NMR spectra were recorded at 62.896 MHz with a Bruker AC 250 MHz Fourier-transform spectrometer. Data [typically $(4-5) \times 10^4$ transients] were recorded at 297 K using a pulse width of 2 μs (45°), sweep width 2000 Hz, and 8K data points (zero-filled to 32K data before Fourier transformation; digitiser resolution 0.122 Hz/point in the final spectrum). Under these conditions the acquisition time is 1.024 s per free induction decay, and a relaxation delay between pulses was not found to be necessary. Chemical shifts are reported on the δ scale with reference to internal 1,4-dioxane at $\delta=67.4$ ppm.

Photolysis procedures. All photolyses were carried out at 25°C in 1 cm cylindrical quartz cells, and the solutions were irradiated at 366 nm. The equipment used was that de-

scribed earlier.⁶ The intensity of the lamp was 4.15×10^{-6} einstein min^{-1} .

Preparation of solutions for photolysis experiments. Most solutions were prepared by directly dissolving the solid compounds in aqueous 0.01 M HClO_4 , containing 20% in D_2O (lock solvent), to give about 13 mM solutions. The *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)(\text{OH}_2)]^{3+}$ solution was made by heating the nitrate complex in the reaction medium at 80°C for 1 h prior to irradiation and ^{13}C NMR measurements.

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