

The standard was Rh(CO)Cl(PPh₃)₂. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. A Cary 17 spectrophotometer was used to obtain the electronic spectra.

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Photochemical Synthesis of *cis*-Chlorobis(ethylenediamine)(ethylenediaminium)rhodium(III) Chloride, *cis*-[Rh(en)₂(enH)Cl]Cl₃·2H₂O

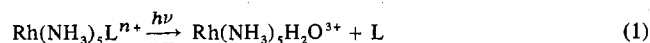
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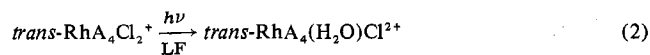
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Ligand field photolysis of Rh(en)₃³⁺ in acidic, chloride media leads to the formation of the monodentate ethylenediamine complex *cis*-Rh(en)₂(enH)Cl³⁺ as the sole photolysis product. The quantum yield for this process is relatively insensitive to acid concentration (1 M > [H⁺] > 10⁻⁸ M) and has a value of ~0.040 mol/einstein. In basic solution (pH > 8), the photolysis product is the deprotonated complex *cis*-Rh(en)₂(mono-en)Cl³⁺. There is no evidence for secondary photochemical or thermal reactions with pH is ≤ 10. These results are discussed in the context of previous mechanistic interpretations of the photochemistry of rhodium(III) amine complexes.

Ligand field photolysis of rhodium(III) amine complexes in aqueous solution customarily leads to photoaquation of one of the ligands in the complex¹ resulting in a monoquo species. Subsequent reactions are not observed spectroscopically since further reaction is usually limited to H₂O exchange.² Some of the literature systems are illustrated by eq 1 and 2.



L = NH₃,³ substituted pyridines,⁴ organonitriles,⁴ Cl⁵



A₄ = (NH₃)₄,⁶ (en)₂,⁶ cyclam⁶

There have been mechanisms proposed for some photochemical⁷⁻¹⁰ and thermal^{11,12} reactions of transition metal complexes in which the bidentate ethylenediamine appears in the product as the monodentate ethylenediaminium ligand. Of these reactions, the only isolated solid for a d⁶ metal system

has been *cis*-[Co(en)₂(enH)Cl]Cl₃·H₂O⁵ which was characterized by elemental analysis and electronic spectroscopy. In addition, there have been some photochemical studies of Rh(III)^{13,14} and Co(III)^{15,16} complexes of ethylenediamine in which a monodentate ethylenediamine ligand has been proposed as an intermediate in the photosubstitution process. Some of these researchers^{13,15,16} have proposed mechanisms in which the labilized end of an ethylenediamine undergoes an edge displacement of a chloro ligand.

The different modes of reactivity of the monodentate ethylenediamine ligand, which apparently either exist as stable species⁷⁻¹² or undergo rechelation through edge displacement of an adjacent chloro ligand,¹³⁻¹⁶ must be a result of subtle changes in the complexes which were studied or must be indicative of an incorrect mechanistic description in some of the earlier work. The tendency of hexaammine-, pentaammine-, and *trans*-dichlorotetraamminerhodium(III) species to undergo photosubstitution at only one coordination site led us to study the ligand field photochemistry of tris(ethylene-

Table I. Absorption Spectra of Some Rh(III) Complexes

Complex ion	λ_{\max} , nm	ϵ_{\max} , M ⁻¹ cm ⁻¹	Ref
Rh(NH ₃) ₆ ³⁺	305	134	10
	255	101	
Rh(en) ₃ ³⁺	301	238	9
	255	191	
Rh(NH ₃) ₅ Cl ²⁺	345	103	a
	277	109	
<i>cis</i> -Rh(en) ₂ (enH)Cl ³⁺	345	140	b
	277	239	

a S. N. Anderson and F. Basolo, *Inorg. Synth.*, 7, 214 (1963).

b This work.

diamine)rhodium(III), Rh(en)₃³⁺, in an attempt to prepare photochemically a complex containing a monodentate ethylenediamine ligand. The choice of chloride as a trapping agent for the coordination site vacated by the formation of a monodentate ethylenediamine ligand arose from the following factors: (1) if the photolysis product, Rh(en)₂(enH)Cl³⁺, behaves similar photochemically to Rh(NH₃)₅Cl²⁺,⁵ secondary photolysis should involve only chloro ligand exchange; (2) in the edge displacement mechanism previously proposed,¹³⁻¹⁶ it was a chloro ligand which was displaced by the free end of the monodentate ethylenediamine ligand.

Experimental Section

Syntheses. [Rh(en)₃]Cl₃·3H₂O. The tris(ethylenediamine) complex was prepared by the standard literature procedure.¹⁷

cis-[Rh(en)₂(enH)Cl]Cl₃·2H₂O. A 0.5-g (1.1-mmol) sample of [Rh(en)₃]Cl₃·3H₂O was dissolved in 35 mL of deoxygenated 1 M 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-X1). 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)₃³⁺) 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 predominantly 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)₃³⁺, a loss in absorbance at 345 nm and an increase in absorbance at 406 nm result. Ion-exchange chromatography (Dowex 50W-X4), electronic spectroscopy,¹⁸ and carbon-13 NMR spectroscopy¹⁹ indicated that the increased absorbance at 406 nm was due to a secondary reaction resulting in the formation of *trans*-Rh(en)₂Cl₂⁺. Isolation of reasonably pure *cis*-[Rh(en)₂(enH)Cl]Cl₃·2H₂O was accomplished by minimizing the secondary processes and recrystallizing from 1 M HCl (photoproduct more soluble in 1 M HCl than Rh(en)₃³⁺).

Anal. Calcd for C₆H₂₅N₆Cl₄Rh·2H₂O: C, 15.6; H, 6.3; N, 18.2; Cl, 30.7. Found: C, 15.6; H, 6.5; N, 18.4; Cl, 32.8.

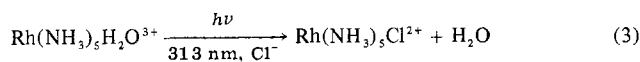
The carbon-13 NMR spectrum^{19b} of *cis*-[Rh(en)₂(enH)Cl]Cl₃·2H₂O was recorded on a Varian XL-100 spectrometer equipped with a Nicolet TT-100 Data System operating at 25.2 MHz. The electronic absorption spectrum and molar extinction coefficients appear in Table I along with selected spectra for other rhodium(III) amine complexes.

Photolysis. Quantitative photolyses of Rh(en)₃³⁺ were carried out using an Oriol Universal Arc Lamp Source with a 200-W high-pressure HgXe lamp and an Oriol G-521-3130 313-nm interference filter. The photolysis procedures and data treatment have been described

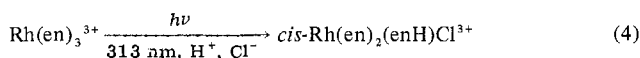
previously.²⁻⁴ Simultaneous determinations for the formation of *cis*-Rh(en)₂(enH)Cl³⁺ and for the consumption of protons were carried out on solutions which were initially 2.33 × 10⁻³ M in Rh(en)₃³⁺ and 7.59 × 10⁻⁴ M in H⁺.

Results and Discussion

The spectrum of Rh(en)₃³⁺ in aqueous solution displays two absorption bands centered at 301 nm (ϵ 238 M⁻¹ cm⁻¹) and 255 nm (ϵ 191 M⁻¹ cm⁻¹).¹⁷ The maxima of these bands are very similar in wavelength to the octahedral complex Rh(NH₃)₆³⁺ (Table I). Photolysis of Rh(NH₃)₆³⁺ at 313 nm³ leads solely to the formation of Rh(NH₃)₅H₂O³⁺ (eq 1), while photolysis of Rh(NH₃)₅H₂O³⁺ at 313 nm in aqueous chloride media leads to photoanation processes² (eq 3). The photo-



chemistry of Rh(en)₃³⁺ (eq 4) appears to parallel the Rh-



(NH₃)₆³⁺ system (eq 1 and 3). The postulation of *cis*-Rh(en)₂(enH)Cl³⁺ as the photoproduct obtained from irradiation of Rh(en)₃³⁺ was made on the basis of the following considerations: (1) The similarity in the electronic band maxima between the photoproduct and Rh(NH₃)₅Cl²⁺ (Table I) suggests that five amine groups and one chloro group are bound to Rh(III) in the photoproduct. (The product is not formed in chloride-free solutions.) (2) The spectroscopic determination of moles of photolysis product vs. moles of protons consumed (measured by pH change) corresponds to a 1:1 ratio. This is consistent with a monoprotonated ethylenediamine in the photolysis product (Table II). (3) Elemental analysis is most consistent with four chlorides per Rh(III) which suggests either an ethylenediaminium ligand or an HCl of solvation is present in the isolated salt. (4) When a mixture of Rh(en)₃³⁺ and the photoproduct are passed through an ion-exchange column (Dowex 50W-X4), both species are eluted together (2.5 M HCl). This implies that both ions have a +3 charge. (5) The photoproduct at pH 8 is identical spectroscopically with the product at pH 0. At 1 M HCl concentrations, any noncoordinated aliphatic primary amines should be protonated. (6) The *cis* geometry for Rh(en)₂(enH)Cl³⁺ is assigned on the basis of the proton-decoupled, carbon-13 NMR spectrum. Six lines are observed²⁰ for the six chemically unique carbon atoms at 47.15, 46.57, 46.00, 45.94, 43.30, and 40.59 ppm. Only three lines are expected for the *trans* complex.²¹ (The related Rh(III) species, *cis*-Rh(en)₂Cl₂⁺, *trans*-Rh(en)₂Cl₂⁺, and *trans*-Rh(en)₂(NH₃)Cl₂²⁺, show two,^{19b} one,¹⁹ and one^{19b} carbon resonances, respectively.)

The quantum yields for the formation of *cis*-Rh(en)₂(enH)Cl³⁺ at 313 nm in aqueous chloride solutions are listed in Table III. It was found that the quantum yield and the nature of the photoproduct are independent of acid concentration (0 ≤ pH ≤ 8). Figure 1 displays a typical photolysis sample vs. thermal sample reaction plot for various irradiation times. The longest exposure time corresponds to approximately 20% reaction. Clean isosbestic points (323, 285, 267, and 244

Table II. Simultaneous Determination for the Photochemical Formation of *cis*-Rh(en)₂(enH)Cl³⁺ and Consumption of Protons

Expt	Amt, mmol				
	Rh(en) ₃ ³⁺ , initial ^a	<i>cis</i> -Rh(en) ₂ (enH)Cl ³⁺ , final ^b	H ⁺ , initial ^c	H ⁺ , final ^d	H ⁺ , consumed ^e
1	14.0	1.8	4.6	2.7	1.9
2	14.0	2.3	4.6	2.3	2.3

^a Initial amount of Rh(en)₃³⁺ in the 6-mL photolysis cell (measured gravimetrically and confirmed spectrophotometrically). ^b Amount of photolysis product, *cis*-Rh(en)₂(enH)Cl³⁺, at the end of the experiment (measured spectrometrically). ^c Initial acid (pH measurement).

^d Final acid (pH measurement). ^e Acid consumed during photolysis (H⁺, initial - H⁺, final).

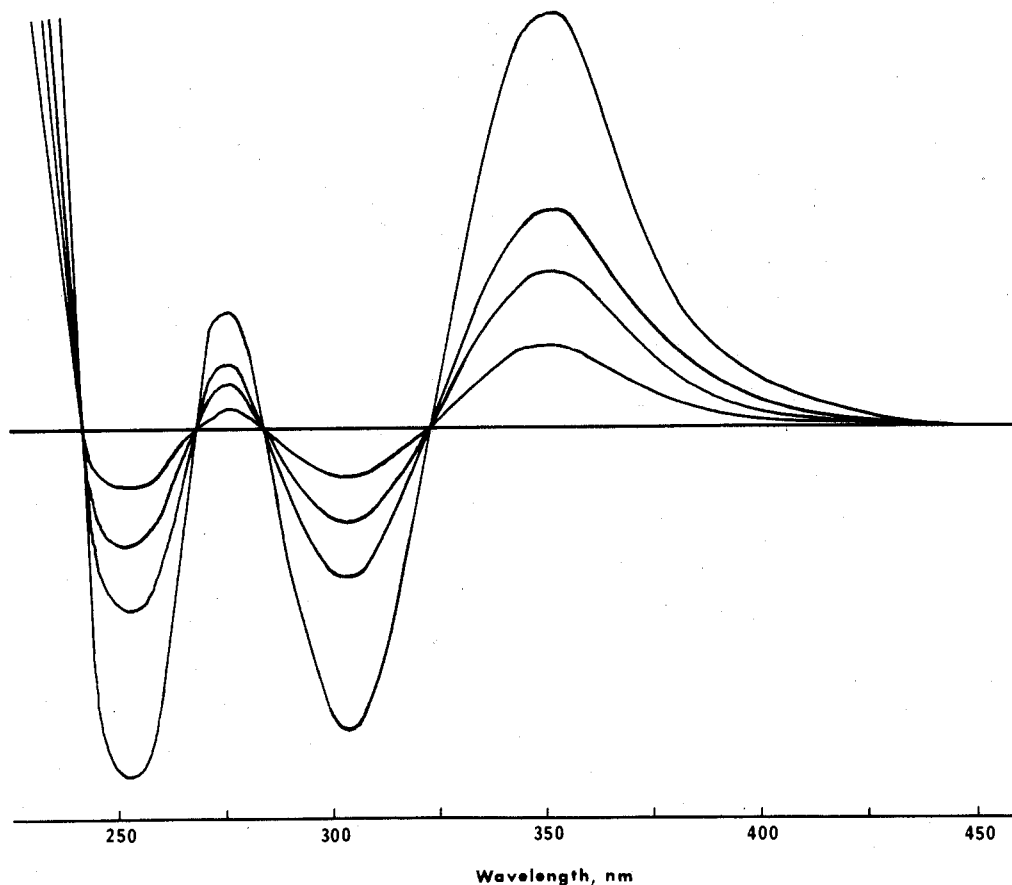


Figure 1. Photolysis sample vs. dark reference as a function of irradiation time for the irradiation of $\text{Rh}(\text{en})_3^{3+}$ at 313 nm. Positive absorbance changes at ~ 350 nm are due to formation of the photolysis product, *cis*- $\text{Rh}(\text{en})_2(\text{enH})\text{Cl}^{3+}$. Negative absorbance changes at ~ 255 and ~ 305 nm are due to depletion of starting material, $\text{Rh}(\text{en})_3^{3+}$.

Table III. Photochemical Quantum Yields for the Formation of *cis*- $\text{Rh}(\text{en})_2(\text{enH})\text{Cl}^{3+}$ at 313 nm (1 M Cl⁻, 25 °C)

pH	Φ_{formn}^a	pH	Φ_{formn}^a
0	0.041 ± 0.004 (4)	8	0.038 ± 0.007 (2)
2	0.042 ± 0.006 (5)	10	0.039 ± 0.003 (2) ^b
4	0.045 ± 0.003 (2)	12	0.035 ± 0.01 (2) ^c
6	0.037 ± 0.003 (2)		

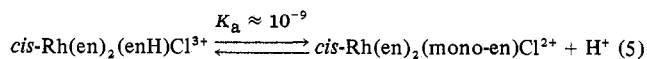
^a Quantum yield (initial) for formation of *cis*- $\text{Rh}(\text{en})_2(\text{enH})\text{Cl}^{3+}$; mean value and average deviation reported with number of determinations in parentheses. ^b Shifting of isobestic points at 263 and 244 nm. ^c Loss of isobestic points.

nm) indicate that no secondary photochemical reactions or thermal reactions of the product are taking place. When a 2.5×10^{-3} M solution (pH 2, 1 M Cl⁻) of $\text{Rh}(\text{en})_3^{3+}$ is photolyzed to >90% reaction, the resulting solution has bands at 345 and 278 nm with molar extinction coefficients (after attempting to correct for the remaining $\text{Rh}(\text{en})_3^{3+}$ and a small amount of *trans*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ formed)²² of 132 and 197 M⁻¹ cm⁻¹, respectively. The extinction coefficient at 345 nm (where the smaller correction was necessary) is within 6% of the value listed in Table I for *cis*-[$\text{Rh}(\text{en})_2(\text{enH})\text{Cl}$]Cl₃·2H₂O.

The 1:1 ratio of the formation of *cis*- $\text{Rh}(\text{en})_2(\text{enH})\text{Cl}^{3+}$ to the consumption of protons (Table II) and the presence of isobestic points during the photolysis reaction (Figure 1) indicate that the quantum yield for formation of *cis*- $\text{Rh}(\text{en})_2(\text{enH})\text{Cl}^{3+}$ is equal to the quantum yield for degradation of $\text{Rh}(\text{en})_3^{3+}$ in acidic chloride media. It is not surprising that 1 M chloride is an efficient scavenger for the open coordination site, even when competing with ~ 55 M water. Monacelli²³ has shown that the ion-pair equilibrium constant for the +3 species, $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, with Cl⁻ is 0.16 M⁻¹. Data on the photoanation of $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$,² in 1 M Cl⁻, indicate that

63% of the $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ formed occurs via an exchange in the ion pair and the quantum yield for the photoexchange of the ion pair is close to unity.

The photolysis reactions of $\text{Rh}(\text{en})_3^{3+}$ in chloride media display isobestic points throughout the acid concentration range $0 \leq \text{pH} \leq 10$. However, there is a red shift in the isobestic points at 263 and 244 nm for photolysis at pH 10. This shift in isobestic points is interpreted as the result of the acid-base equilibrium for the protonated-deprotonated form of the monodentate ethylenediamine. Calculations from photolysis spectra place the pK_a of the monocoordinated amine at 9 ± 1 . (See eq 5.) Muir and Huang¹³ have studied the



photochemistry of *cis*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ which underwent photoaquation of chloride and/or photoisomerization to trans products. One of the proposed mechanisms¹³ for photoisomerization involved the formation of a monodentate ethylenediamine group. This process now appears unlikely since, at neutral pHs, the monocoordinated amine should be protonated to give *cis*- $\text{Rh}(\text{en})(\text{enH})(\text{H}_2\text{O})\text{Cl}_2^{2+}$ (pK_a should be smaller for $\text{Rh}(\text{en})_2(\text{enH})\text{Cl}^{3+}$ due to charge differences). Our results, in which no edge displacement of chloride by monodentate ethylenediamine occurs (even in basic solution) causing a return to $\text{Rh}(\text{en})_3^{3+}$, would indicate that all of the photoisomerization in *cis*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ ($\Phi_{\text{isom}} \approx 0.11$)¹³ must be occurring without the breaking of a Rh-N bond. Thus photoisomerization of *cis*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ must be occurring via initial loss of Cl⁻ followed by rearrangement to give *trans*- $\text{Rh}(\text{en})_2(\text{H}_2\text{O})\text{Cl}_2^{2+}$.²⁴ These data are consistent with recent work by Ford and Strauss²⁵ in which irradiation of the lowest ligand field band of aqueous *cis*- $\text{Rh}(\text{NH}_3)_4\text{Cl}_2^+$ leads cleanly

to formation of *trans*-Rh(NH₃)₄(H₂O)Cl²⁺ with a quantum yield of 0.38 mol/einstein.

The retention of stereochemistry in the photolysis of Rh(en)₃³⁺ to form *cis*-Rh(en)₂(enH)Cl³⁺ and the presence of *trans*-Rh(en)₂Cl₂⁺ as a secondary photolysis product indicate that the photocatalyzed exchange of Cl⁻ for enH⁺ (second step) is proceeding through an excited-state rearrangement. If a dissociative intermediate is proposed for both the photoanation of *cis*-Rh(en)₂(enH)Cl³⁺ and the photoaquation of *cis*-Rh(en)₂Cl₂⁺, the five-coordinate intermediate (Rh(en)₂Cl₂²⁺ in both cases) shows a 100% efficiency toward rearrangement so that the incoming ligand enters *trans* to Cl. This rearrangement must depend on the presence of the chloro ligand and not the two bidentate ethylenediamine ligands in the five-coordinate intermediate since the photolysis of Rh(en)₃³⁺ leads solely to a *cis* product.

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Registry No. *cis*-[Rh(en)₂(enH)Cl]Cl₃, 63744-43-4; [Rh(en)₃]Cl₃, 14023-02-0; ¹³C, 14762-74-4.

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- Small peaks due to unreacted starting material, Rh(en)₃³⁺ (46.36 ppm), and secondary photolysis product, *trans*-Rh(en)₂Cl₂⁺ (45.68 ppm), are observed in addition to the six peaks of the *cis*-Rh(en)₂(enH)Cl³⁺. These impurities were confirmed by spiking the sample with the two impurities. The two impurity peaks could be removed by computer subtraction techniques using authentic spectra of Rh(en)₃³⁺ and *trans*-Rh(en)₂Cl₂⁺.
- Interchange between the λ and δ conformations of the bidentate ethylenediamine should be rapid on the NMR time scale and should not result in magnetic nonequivalence due to ring confirmation [see E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959)].
- Corrections were made spectroscopically by Gaussian curve shape analysis. Concentrations of *trans*-Rh(en)₂Cl₂⁺ (5–7%) were determined from a well-defined shoulder at 406 nm while concentrations of Rh(en)₃³⁺ (<2%) were calculated from a very small shoulder on the long-wavelength side of the 277-nm band in the photolysis product.
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- Muir and Huang¹³ observed some *trans*-Rh(en)₂Cl₂⁺ in photolyzed solutions of *cis*-Rh(en)₂Cl₂⁺ and postulated that *cis* → *trans* isomerization of the dichloro species may be the primary photolysis step. A recent ¹³C NMR study^{19b} indicates that the *cis*-Rh(en)₂Cl₂⁺ used in this study was probably a mixture containing 80% *cis* isomer and 20% *trans* isomer.
- P. C. Ford, private communication.

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Rhodium Atom Chemistry. 1. Synthesis and Characterization of Dirhodium, Bis(dioxygen)rhodium, and Mono(dioxygen)rhodium

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Optical spectra from 200 to 900 nm have been obtained for Rh atoms in Ar, Kr, and Xe matrices at 10–12 K and are found to correlate reasonably well with the reported gas-phase atomic transitions. The metal concentration and matrix conditions which favor the dimerization of Rh atoms to Rh₂ molecules are quantitatively assessed using optical spectroscopy. The metal clustering that occurs during the matrix deposition process is analyzed in terms of a simple kinetic theory which enables small metal aggregates to be identified in the presence of atomic species. An earlier report of spectra ascribed to Rh atoms isolated in Ne matrices is shown from this study to be more consistent with a mixture of Rh and Rh₂ dimers. With this background information the cocondensation reactions of Rh atoms with O₂ and O₂/inert gas matrices at 10–12 K are investigated under conditions which favor *mononuclear* complex formation (rhodium cluster-dioxygen complexes constitute the subject of part 2 of this study). The infrared spectra recorded under these circumstances indicate that two dioxygen complexes can be generated. These are established from ¹⁶O₂/¹⁸O₂ and ¹⁶O₂/¹⁶O¹⁸O/¹⁸O₂ isotopic substitution experiments to be Rh(O₂)₂ and Rh(O₂). The corresponding ¹⁶O¹⁸O infrared data spectroscopically indicate that the dioxygen moieties in both complexes are bonded to the rhodium atom in a dihapto (side-on) fashion. The UV-visible spectrum of Rh(O₂)₂ is recorded in O₂ matrices and is compared with that for the isostructural Pd(O₂)₂ complex. In an effort to understand the electronic structures of these interesting bis(dioxygen) complexes and the origin of the shifts in their UV absorptions, extended Hückel molecular orbital calculations are undertaken. An argument which favors a bis-superoxide formulation and an O₂ → M charge-transfer assignment for the observed UV bands of Rh(O₂)₂ and Pd(O₂)₂ is presented.

Introduction

The cryochemically controlled manipulation of metal atom reactions with themselves and with other molecules has pointed the way to a fundamental new method of examining small, well-defined "naked" metal clusters and "localized bonding"

aspects of surface molecular states.¹ In particular, our recent thrust toward modeling catalytic intermediates on atomic, diatomic, and higher order metal cluster sites and relating the data to the chemisorbed state is beginning to yield intriguing new information about metal-ligand (pseudo-adsorbate-ad-