

15121-26-3; deuterium, 7782-39-0; *trans*-[Co(NH₃)₄(ND₃)₂O₂CCH₃](ClO₄)₂, 55449-62-2.

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Chemical Behavior of Rhodium(II)-Ammine Complexes Generated by the Pulse Radiolytic One-Electron Reduction of Rhodium(III) Amines

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The pulse radiolytic reduction of Rh(NH₃)₅Cl²⁺, Rh(NH₃)₅OH₂³⁺, Rh(NH₃)₄Br²⁺ by the hydrated electron has been examined. The first two ligands of the product rhodium(II) complex are eliminated very fast (<1 μsec), and the first intermediate identified is a Rh(NH₃)₄²⁺ species. This further exchanges ammonia for water with $k = 3.5 \times 10^2 \text{ sec}^{-1}$ for the first NH₃ and with $k = 40 \text{ sec}^{-1}$ for the second NH₃. In addition, Rh(NH₃)₄²⁺ appears to disproportionate with $k = 1.4 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. It reacts with oxygen with $k = 3.1 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ forming a dioxygen adduct, O₂Rh(NH₃)₄OH₂²⁺, which is relatively stable and has an absorption maximum at 265 nm with an absorptivity of 9200 M⁻¹ cm⁻¹. The Rh(NH₃)₄²⁺ reduction of Rh(NH₃)₄Br²⁺ results in a chain reaction that catalyzes the exchange of Br⁻ for H₂O in the rhodium(III) substrate.

Introduction

The d⁷ electronic configuration is notoriously rare among monomeric transition metal complexes, with the known examples being overwhelmingly complexes of cobalt(II).^{2,3} Among low-spin cobalt(II) complexes two different coordination geometries have been established: (a) five-coordinate as in Co(CN)₅³⁻ and (b) axially distorted six-coordinate as in Co^{II}(N₄)X₂ (N₄ = a cyclic tetraamine, porphyrin, etc.) species. In their solution chemistry, these low-spin cobalt(II) species are labile to substitution in one or more axial positions,⁶ and they exhibit little affinity for binding of ligands in these labile axial positions.⁶ Ammine complexes of cobalt(II) tend to be high spin and labile in all coordination positions;^{7,8} however, one would expect the heavy-metal analogs, e.g., ammine complexes of rhodium(II), to be low spin and related in lability to one of the classes of low-spin cobalt(II) complexes.

A small number of rhodium(II) complexes have been investigated. The few rhodium(II) complexes which have been isolated as solids have been dimer, exhibiting a strong metal-metal bond,^{2,9} thus providing no basis for discussing the solution chemistry of monomeric rhodium(II) species. On the other hand, monomeric rhodium(II) species have been postulated as transient intermediates in electron transfer¹⁰ and

photochemical^{11,12} reactions of rhodium(III) complexes in aqueous solution.

The rhodium(II) species produced in photoredox reactions of rhodium(III) complexes tend to be very short-lived since they are good reducing agents, necessarily generated in the presence of radical oxidants.^{11,13} As a consequence it is difficult to develop good criteria for the intermediacy of rhodium(II) in these systems, especially in the absence of definitive information concerning the chemistry of such species. In connection with their study of the photoredox chemistry of Rh(NH₃)₅I²⁺, Kelly and Endicott suggested that rhodium(II) species were axially labile in two coordination positions, analogous to the axially distorted Co^{II}(N₄)X₂ species mentioned above. This suggestion was based on studies of the intermediates (I₂⁻) and the products of tetraamminerhodium(III) species) resulting from photolysis of iodide solutions containing nonabsorbing amounts of Rh(NH₃)₅OH₂³⁺; it was argued that the reactive rhodium(II) species were generated by rhodium(III) scavenging of the electrons from iodide photolysis, then oxidized by iodine radicals (or molecules). Thus these authors proposed that generation of tetraammine rhodium species was a necessary criterion for the intermediacy of rhodium(II). This proposal has been disputed by Basolo and

Table I. Rate Constants of e_{aq}^- Reacting with Some Rhodium Complexes Obtained from the Decay Rates of e_{aq}^- at 700 nm^a

Complex	$10^5 c, M$	pH	$10^{-10} k, M^{-1} \text{ sec}^{-1}$
$\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$	5.9	6.3	6.7
$\text{Rh}(\text{NH}_3)_5\text{OH}_2^{3+}$	4.0	5.8	7.9
$\text{Rh}(\text{NH}_3)_5\text{N}_3^{2+}$	4.6	6.1	7.3
$\text{Rh}(\text{NH}_3)_4\text{Br}_2^+$	4.2	6.4	6.9

^a The solutions contained $10^{-2} M$ *tert*-butyl alcohol to scavenge OH radicals and all counterions were ClO_4^- .

coworkers,¹² who proposed that pentaamminerhodium(II) species and azide radicals were among the products resulting from ultraviolet irradiations of $\text{Rh}(\text{NH}_3)_5\text{N}_3^{2+}$; this proposal suggests that amminerhodium(II) complexes behave more like $\text{Co}(\text{CN})_5^{3-}$ than the low-spin axially distorted $\text{Co}^{\text{II}}(\text{N}_4)\text{X}_2$ species. In view of these contradictory claims for the chemical behavior of rhodium(II) it seemed appropriate to undertake a specific study of the lability of rhodium(II) complexes. We have done this using the pulse radiolysis method to generate rhodium(II) species.

Pulse radiolysis has become a useful tool in the study of fast redox processes and has advantages over stopped flow for studies of very rapid reactions of metal complexes. In a recent publication⁸ kinetic conductivity coupled to pulse radiolysis was introduced in the study of ligand-exchange kinetics. This technique is applicable whenever specific conductivity changes take place and has many advantages over the kinetic spectrophotometric detection system since in many cases the intermediates do not have strong or characteristic absorbances. We have used this approach in the kinetic study of the reactions which follow the reduction of some rhodium(III) complexes. Rhodium(III) complexes are stable and have an octahedral structure. On the other hand, the rhodium(II) complexes are in general unstable; we shall see below that the lifetimes of unstable rhodium(II) complexes produced on reduction by hydrated electrons, e_{aq}^- , are within the time resolution of the techniques used ($< 1 \mu\text{sec}$).

Experimental Section

In the pulse radiolysis of aqueous solutions the primary species are as indicated in (1) with relative yields, G values, i.e., number of $\text{H}_2\text{O} \rightsquigarrow e_{aq}^-$ (2.7), H_3O^+ (2.7), OH (2.7), H (0.6), H_2O_2 (0.5) (1)

molecules per 100 eV of radiation absorbed indicated in parentheses. In the experiments reported here the OH radicals and H atoms were removed by added 2-methyl-2-propanol (0.5 M); this left the hydrated electrons to react with the complexes. For the rhodium(III) complexes used in this study, the rates of reaction with e_{aq}^- are diffusion controlled (see Table I).

The solutions were made up with ultrapure water from a Millipore system. All chemicals were of highest commercial grade. Rhodium complexes were prepared from commercial $\text{Rh}(\text{NH}_3)_5\text{Cl}^{3+}$ (Matthey-Bishop, Inc.) and purified as described previously.^{11,15} Oxygen was eliminated by purging with O_2 -free argon. The complexes were added to purged solutions and pulsed immediately. The solutions were not exposed to light in order to avoid photolysis. Oxygenated solutions were prepared similarly except that the desired O_2 concentration was achieved by addition of required volume of O_2 -saturated water.

The pulse radiolysis equipment (1.6-MeV electrons from a Van de Graaff generator, pulse duration 0.5 μsec) and the 10-MHz kinetic conductivity technique have been described.^{16,17} The dose and the conductivity cell constant were always determined before a run of experiments using $10^{-4} M$ tetranitromethane solutions in presence of $10^{-2} M$ 2-propanol.¹⁸ The dose was calculated from $G(\text{C}(\text{NO}_2)_3^-) = 6.0$ and $\epsilon(\text{C}(\text{NO}_2)_3^-) = 14,000 M^{-1} \text{ cm}^{-1}$ at 350 nm.¹⁹ The cell constant was calculated from equivalent conductivities:²⁰ $\Lambda(\text{H}_3\text{O}^+) = 350 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ and $\Lambda(\text{C}(\text{NO}_2)_3^-) = 40 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ all at 25°. The equivalent conductivities of the intermediates were calculated from the dose per pulse and $G(e_{aq}^-) = 2.7$. In most of the experiments 500 rads/pulse was sufficient which corresponds to 1.3×10^{-6} mol of hydrated electrons per pulse.

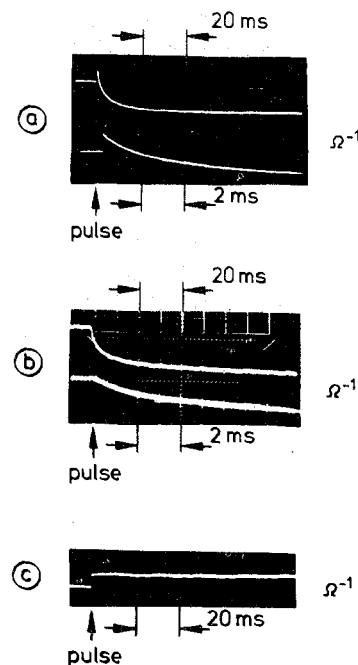


Figure 1. Conductivity in an oxygen-free solution of 0.5 M 2-methyl-2-propanol with (a) $10^{-3} M$ $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, (b) $10^{-3} M$ $\text{Rh}(\text{NH}_3)_5\text{OH}_2^{3+}$, and (c) as (a) but with $2 \times 10^{-5} M \text{ O}_2$; pH 4.0.

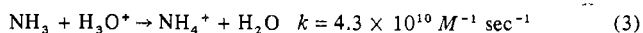
Most of the experiments were done only with kinetic conductivity since illumination of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Rh}(\text{NH}_3)_4\text{Br}_2^+$ solutions by the Xe lamp of the optical detection system resulted in immediate conductivity changes. Only the $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ solutions were relatively stable and analyzing light could be applied. Hence the intermediates of the latter complex were also investigated by kinetic spectrophotometry.

The time-dependent signals from both conductivity and spectrophotometric technique were stored in a Biomation 810 transient recorder, transferred automatically to paper tape and evaluated on a PDP 11 computer.

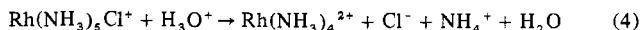
Results and Discussion

A. Formation of $\text{Rh}(\text{NH}_3)_4^{2+}$. In $10^{-3} M$ solutions of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, the reaction with hydrated electrons (2) is over $e_{aq}^- + \text{Rh}(\text{NH}_3)_5\text{Cl}^{2+} \rightarrow \text{Rh}(\text{NH}_3)_4^{2+} + \text{Cl}^-$ (2)
 $k = 6.7 \times 10^{10} M^{-1} \text{ sec}^{-1}$

at the end of the pulse (0.5 μsec). Rates for some other Rh complexes are given in Table I, and all of them are extremely fast. At this time the conductivity is expected to correspond to one proton ($\Lambda = 350 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)²⁰ and $\text{Rh}(\text{NH}_3)_5\text{Cl}^+$ ($\Lambda = 50 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)²⁰ for every hydrated electron produced (eq 1). Figure 1a shows the oscilloscope trace of the observed conductivity with $\Delta\Lambda = 120 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ immediately after the pulse. The conductivity then decays to a value below zero (the initial conductivity). These observations can be accounted for on the basis of reaction schemes similar to those previously proposed for $\text{Co}(\text{NH}_3)_5\text{Cl}^+$ ⁸ and the corresponding conductivity changes (eq 1). Thus, if one ammonia and the chloride are rapidly displaced from coordination in the reduced complex, $\text{Rh}(\text{NH}_3)_5\text{Cl}^+$, the ammonia would be rapidly ($< 1 \mu\text{sec}$) protonated (eq 3), contributing a change in conductivity



of $-270 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Then the overall reaction following reaction 2 with e_{aq}^- is given by (4) where it is understood that



the "vacant" coordination positions on the rhodium(II) species could be filled by solvent species whose identity is unknown owing to the lability of these positions. The conductivity change

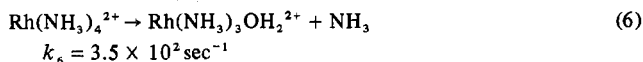
caused by the pulse after the reaction of e_{aq}^- is attributed to the loss of H_3O^+ conductivity and the formation of Cl^- ($\Lambda = 76 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and NH_4^+ ($\Lambda = 74 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). The conductivity change caused by the replacement of $Rh(NH_3)_5Cl^{2+}$ by $Rh(NH_3)_4^{2+}$ is negligible because both ions have approximately the same equivalent conductivity. The calculated $\Delta\Lambda = 150 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ is in good agreement with the observed value $\Delta\Lambda = 120 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Similar analysis applies to the reduction of $Rh(NH_3)_5OH_2^{3+}$. The observed initial conductivity change is here $\Delta\Lambda = 10 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ somewhat different than in the above case owing to the expected difference in mobilities of $Rh(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_4^{2+}$ and to the absence of Cl^- conductivity. The overall reaction following the reduction by hydrated electrons is given by (5). The conductivity changes

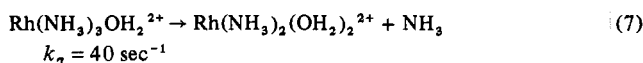


are expected to be negligible since the conductivities of $Rh(NH_3)_4^{2+}$ and NH_4^+ should approximate that of $Rh(NH_3)_5OH_2^{3+}$. In these experiments no optical absorption ($\epsilon < 200 M^{-1} \text{ cm}^{-1}$) could be detected of $Rh(NH_3)_4^{2+}$ from 250 nm to the visible region.

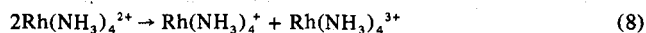
B. Decay of $Rh(NH_3)_4^{2+}$. As we have seen above, $Rh(NH_3)_4^{2+}$ species can be easily formed on reduction of certain rhodium(III) complexes and the lifetime of such species is much longer than $1 \mu\text{sec}$. The conductivity changes at longer times (decay half-lives of 2 and 17 msec) can be attributed to the loss of ammonia ligands as in the case of the $Co(NH_3)_3^{2+}$ intermediates.⁸ The conductivity changes in Figure 1a and 1b follow the same time pattern and the observed $\Delta\Lambda = -400 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ between the time shortly after the pulse, when the $Rh(NH_3)_4^{2+}$ was formed, and the long time beyond which no conductivity changes were observed correspond approximately to the elimination of two NH_3 ($\Delta\Lambda = 275 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for one NH_3). Hence



and



An alternative mechanism based on fast disproportionation and subsequent total hydrolysis of the Rh(II) complex is less likely since no dose rate effect was observed (0.5–3-krad/pulse).



Even if one would assume the largest possible disproportionation rate, $k_8 \approx 10^9 M^{-1} \text{ sec}^{-1}$, the observed decay rate attributable to reaction 9 would be affected for the dose rates used. Since no such effect was observed, it is not likely that the exchange of ligands proceeds via reactions 8 and 9; hence the NH_3 elimination must proceed mainly from the $Rh(NH_3)_4^{2+}$ intermediate (reaction 6). The fact that somewhat less than two NH_3 groups are eliminated from $Rh(NH_3)_4^{2+}$ can be due to an equilibrium in eq 7, but it is more likely that, parallel to reactions 6 and 7, disproportionation (eq 8) to some extent takes place. If this is true, the rate of disproportionation should be comparable to the second hydrolysis step, giving for $10^{-6} M$ Rh(II) a second-order rate of the order of $10^7 M^{-1} \text{ sec}^{-1}$.

Measurements were carried out with added H_2O_2 to see whether the rhodium(II) species could be oxidized by this reagent. The reactions observed were the same as without H_2O_2 for $[H_2O_2] \leq 10^{-4} M$, indicating that there is no rapid oxidation. On the other hand even traces of O_2 affected the decay of $Rh(NH_3)_4^{2+}$ (see section D).

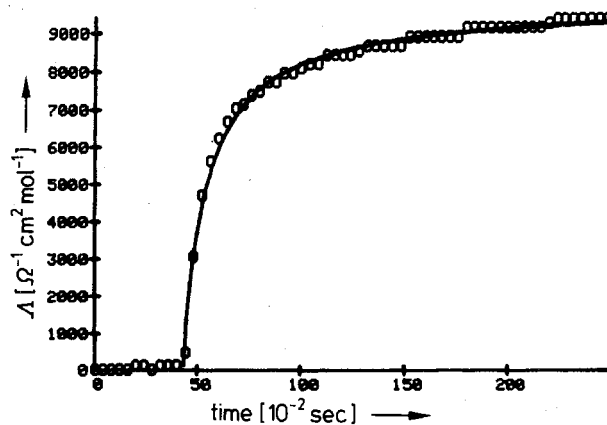
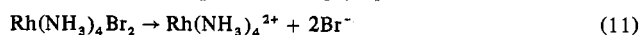
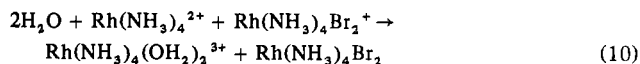


Figure 2. Equivalent conductivity in an oxygen-free solution of $0.5 M$ 2-methyl-2-propanol with $10^{-3} M$ $Rh(NH_3)_4Br_2^+$; pH 4.0.

C. $Rh(NH_3)_4^{2+} + Rh(NH_3)_4Br_2^+$ Reaction. After the reaction of e_{aq}^- with $Rh(NH_3)_4Br_2^+$ immediately after the pulse, an increase in conductivity of $\Delta\Lambda = 500 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ is observed. This corresponds to the presence of H_3O^+ , two Br^- , and $Rh(NH_3)_4^{2+}$. Instead of subsequent decay of this conductivity due to hydrolysis of $Rh(NH_3)_4^{2+}$, as in the previous cases, we observed an enormous increase of conductivity (Figure 2). At 3 sec the "equivalent conductivity" reached a maximum value of $\Lambda = 10,000 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Such a high value can be produced only by a chain reaction in which the ligands of $Rh(NH_3)_4Br_2^+$ are displaced; reactions 10 and 11 are suggested.



As we know from the fast initial increase ($\Delta\Lambda = 500 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$), reaction 11, which is analogous to reaction 4, occurs in $< 1 \mu\text{sec}$. Hence the rate-determining step should be reaction 10. This rate of decomposition of the $Rh(NH_3)_4Br_2^+$ complex may be described by eq 12. From the

$$-dc/dt = k_{10} [Rh(NH_3)_4^{2+}] [Rh(NH_3)_4Br_2^+] \quad (12)$$

initial slope of the conductivity signal we obtain the rate constant $k_{10} \approx 1.4 \times 10^6 M^{-1} \text{ sec}^{-1}$.

The chain length can be estimated from the final conductivity. For $10^{-6} M$ $Rh(NH_3)_4^{2+}$ concentration, the chain length is about 50. Since less than 5% of the initial $Rh(NH_3)_4Br_2^+$ concentration is consumed, the substrate concentration is not the limiting factor. The increase in conductivity is strongly dependent on the dose:pulse, i.e., the $Rh(NH_3)_4^{2+}$ concentration. At higher dose:pulse, $\tau_{1/2}$ and the chain length became shorter. This is indicative of a second-order termination reaction and the most probable ones are the disproportionation or dimerization of $Rh(NH_3)_4^{2+}$. Assuming termination is due to disproportionation and from the $[Rh(NH_3)_4^{2+}]$ dependence of the conductivity, we estimate $k_8 \approx 6 \times 10^6 M^{-1} \text{ sec}^{-1}$. The curve in Figure 2 shows the computer-calculated rise of the conductivity for this value of k_8 and appropriate conditions.

This analysis is complicated by contributions of reaction 3. The hydrolysis of the $Rh(NH_3)_4^{2+}$ takes place parallel to the chain. This reaction gives a decay in conductivity that compensates part of the conductivity increase by reaction 11. Under the conditions reported above ($[Rh(NH_3)_4Br_2^+] = 10^{-3} M$), reaction 10 is 5 times faster than reaction 3 and the formation of NH_4^+ contributes only to a small extent. The triamminerhodium(II) intermediate could exhibit reactions analogous to (1) and (8) for the tetraammine. However, we found no increase in conductivity in a $2 \times 10^{-4} M$ solution of

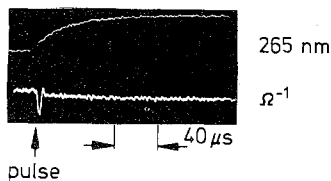
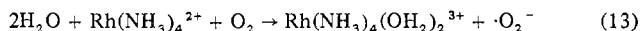


Figure 3. Conductivity and optical absorption (λ 260 nm) in a $2 \times 10^{-5} M$ O_2 -containing solution of $0.5 M$ 2-methyl-2-propanol with $10^{-3} M$ $Rh(NH_3)_5OH_2^{3+}$; pH 4.0.

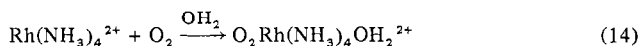
$Rh(NH_3)_4Br_2^+$ above the initial step since the increase due to Br^- formation is just compensated by the decrease by NH_3 protonation.

The chain is effectively inhibited by oxygen (see below). This is important for the preparation of the material since in oxygen-free solutions the chain could easily be started by photolytic charge-transfer excitation and could result in mixtures of complexes.

D. Formation of $O_2Rh(NH_3)_4OH_2^{2+}$. In solutions containing $2 \times 10^{-5} M$ oxygen the initial conductivity observed immediately after the pulse when all of the hydrated electrons have reacted quantitatively with rhodium(III) complexes ($10^{-3} M$) is the same (Figure 1c) as in the absence of O_2 . While in the absence of O_2 the conductivity decreased at longer times, in the presence of O_2 the conductivity did not change at all. We conclude that the displacement of NH_3 from $Rh(NH_3)_4^{2+}$ is efficiently inhibited by O_2 . The constancy of conductivity also eliminates reaction 13 because this would result in an



increased conductivity or, at pH values where the $\cdot O_2^-$ is protonated ($pK = 4.8$),²² a decay in conductivity due to the consumption of protons for the formation of $\cdot O_2H$. The only possible reaction is the addition of O_2 to the rhodium(II) species (eq 14). By analogy with dioxygen adducts of co-



balt(II) this new species could be alternatively formulated as an $\cdot O_2^-$ complex of rhodium(III)²³ or an O_2 complex of rhodium(II).²⁴ The quenched lability of ammonia is most consistent with the superoxyrhodium(III) formulation. This dioxygen adduct must be relatively stable because any reaction forming species such as $Rh(NH_3)_4(OH_2)_2^{3+}$ and H_2O_2 , etc., would result in a conductivity change, and we observed no such changes over periods of several seconds.

In a solution of $10^{-4} M$ $Rh(NH_3)_5OH_2^{3+}$ with *tert*-butyl alcohol and $2 \times 10^{-5} M$ O_2 we found an initial conductivity change of $\Delta\lambda = -10 \Omega^{-1} cm^2 mol^{-1}$ as in the absence of oxygen. There were no further changes in conductivity. Because the $Rh(NH_3)_5OH_2^{3+}$ does not photolyze readily, optical measurements were possible. Figure 3 (upper trace) shows optical absorption changes at 260 nm. The rate was proportional to the oxygen concentration and from pseudo-first-order rate constants and the known O_2 concentrations we find $k_{14} = 3.1 \times 10^8 M^{-1} sec^{-1}$. Because of this relatively large rate constant, even the smallest O_2 concentrations ($10^{-7} M$) compete favorably with the displacement of NH_3 in the $Rh(II)$ intermediate ($\tau_{1/2} = 2$ msec; reaction 6). Figure 4 shows the spectrum that has been measured 200 μ sec after the pulse, when reaction 7 was complete. One sees a strong absorption peak at 265 nm with an extinction coefficient of ϵ 9600 $M^{-1} cm^{-1}$. Irradiating an air-saturated 3 mM $Rh(NH_3)_5OH_2^{3+}$ solution in a cobalt-60 γ source at 8×10^4 rads gave the same spectrum (measured by a Leitz spectrophotometer). The absorption spectrum was stable for several hours.

That k_{14} is about an order of magnitude lower than diffusion controlled suggests weak binding of solvent species in the labile axial positions, similar to the axially distorted $Co^{II}(N_4)X_2$

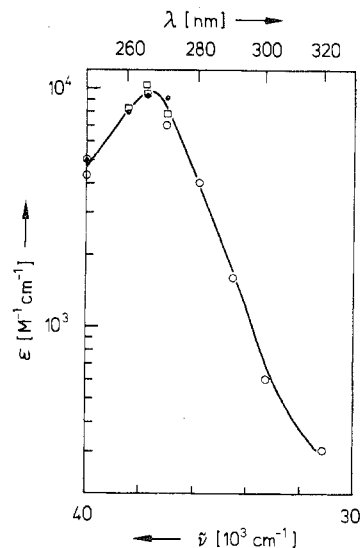


Figure 4. Spectrum 200 μ sec after the pulse in a solution with $2 \times 10^{-5} M$ O_2 , $0.5 M$ 2-methyl-2-propanol, and $10^{-3} M$ $Rh(NH_3)_5OH_2^{3+}$; pH 4.0.

species;⁶ i.e. this rate constant would be consistent with rate-determining dissociation of axially coordinated solvent molecules, with $k_{diss} \approx 2 \times 10^9 sec^{-1}$.²⁵

Conclusions

This study demonstrates that the ligands of six-coordinate rhodium(II) species fall into two classes according to their differences in lability. (1) Two coordination positions are very labile, with the lifetime for dissociation being less than 1 μ sec; upon occupation by water and on the basis of the rate of adduct formation with O_2 , we estimate $k_{diss} \approx 2 \times 10^9 sec^{-1}$. (2) The remaining coordination positions are only labile on a millisecond or longer time scale.

These observations make ammine complexes of rhodium(II) appear to be more similar to axially distorted, low-spin $Co^{II}(N_4)X_2$ species than to $Co(CN)_5^{3-}$. Even the facile adduct formation with O_2 is not rapid enough in air saturated solutions to scavenge for rhodium(II) before two ligands have been displaced. More specifically, it seems unlikely that pentamminerhodium(II) species can be trapped by anything but very concentrated (molar), facile oxidants. It is therefore appropriate to regard the formation of tetraamminerhodium products as a necessary criterion for the intermediacy of rhodium(II) in photochemical reactions (and possibly some redox reactions) of pentaamminerhodium(III) complexes.²⁶

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Registry No. $Rh(NH_3)_5Cl_2^{2+}$, 15379-09-6; $Rh(NH_3)_5OH_2^{3+}$, 15337-79-8; $Rh(NH_3)_5N_3^{2+}$, 21393-76-0; $Rh(NH_3)_4Br_2^+$, 55569-47-6; $Rh(NH_3)_4^{2+}$, 55556-67-7; $O_2Rh(NH_3)_4OH_2^{2+}$, 55556-68-8.

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New Cationic Complexes of Iridium(I), Iridium(III), and Rhodium(III)

H. C. CLARK* and K. J. REIMER

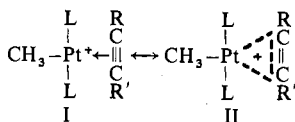
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The syntheses of two new series of cationic Ir(III) and Rh(III) complexes are described: namely, [IrCl(Me)CO-(PMePh₂)₂L]PF₆, where L = CO, carbene, nitrile, or imino ether, and [MCl₂L(PMe₂Ph)₃]PF₆, where M = Ir or Rh and L = H₂O, pyridine, carbene, etc. Their spectroscopic parameters and stereochemistries are described. Two new iridium(I)-acetylene cations have been prepared. Attempts to prepare the Rh(III) analogs of the above methyliridium(III) cations led to cationic acylrhodium species. The applicability of the metal-induced carbonium ion model to account for carbene complex formation from iridium(III)- and rhodium(III)-acetylene complexes is considered.

Introduction

Much of the recent research in this laboratory has dealt with the reactions of organoplatinum cations with unsaturated species such as acetylenes, olefins, isocyanides, and nitriles. It has been found that the course of some of these reactions can be interpreted in terms of a platinum-induced carbonium ion model.¹ Reactivity characteristic of carbonium ions, II, such as intramolecular rearrangement and/or nucleophilic addition is thus observed.



Clearly, this reactivity is directly related to the bonding in these particular compounds and other reactions may occur with different metal complexes.

We have now attempted to apply the concept of metal-induced carbonium ions to complexes of other metals to determine if a system could be designed which would undergo reactions analogous to those of the organoplatinum cations.

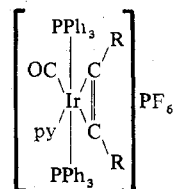
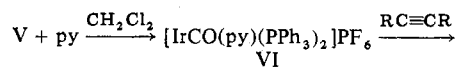
Results and Discussion

A. Reactions of Rhodium(I) and Iridium(I) Complexes. A large number of cationic complexes of rhodium(I) and iridium(I) are known.²⁻¹⁴ Since removal with a silver salt in solution of the chloride ligand in MClCO(PPh₃)₂, III (M = Rh, Ir),⁷ gives [M(CO)(solvent)(PPh₃)₂]⁺, IV, which is isoelectronic with [Pt(Me)(solvent)L₂]⁺, it was of interest to investigate reactions of such cations with acetylenes. However, no products could be isolated from the reaction of methanol or acetone solutions of IV with a variety of di- or mono-substituted acetylenes. Displacement of coordinated acetylenes in the presence of a large excess of oxygen donors (such as

methanol or acetone) was observed for the methylplatinum(II) cations and it is possible that a similar "solvation" effect was operative in these present reactions.

Although III did react with silver hexafluorophosphate in dichloromethane, the reaction was always incomplete unless a small amount of acetone was added to the reaction mixture. In the absence of other donors (such as pyridine) the addition of pentane gave crystals of [MCO(acetone)(PPh₃)₂]PF₆, V. This is a convenient starting material for a large number of compounds, [MCO(L)(PPh₃)₂]PF₆, but no complexes could be isolated from reactions with acetylenes. The addition of acetylenes to dichloromethane solutions of V resulted in intensely colored (red or orange) solutions from which only the unreacted acetone cation could sometimes be recovered. A reaction between ethylene and the iridium-acetone cation afforded a product which appeared analogous to the previously reported¹⁵ complex [IrCO(C₂H₄)₂(PMe₂Ph)₂]⁺.

However, 1:1 adducts were isolated with electrophilic acetylenes if 1 equiv of pyridine was introduced into the reaction mixture before the acetylene addition (eq 1). If the



VII (R = CF₃, CO₂CH₃)

order of addition was reversed, no compound could be isolated from the reaction. Presumably the pyridine discourages al-