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Reactions of the 17-Electron Bis(dimethylglyoximato)(triphenylphosphine)rhodium(II) Radical with Cobalt(III) Complexes

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The rhodium(II) radical $Rh(dmgH)_2PPh_3$, formed by the laser flash photolysis of its dimer, is oxidized by a range of cobalt(III) complexes of the type $XCo(dmgH)_2PPh_3$ and $Co(NH_3)_5X^{2+}$, where X is a halogen or pseudohalogen. The second-order rate constants measured at 23 °C in 95% ethanol for these reactions fall within the range 2.9×10^6–3.0×10^8 L mol^{-1} s^{-1}. For the halides, the "normal" reactivity order is observed, i.e., $Br^- > Cl^- > F^-$. The mechanisms of these reactions are discussed; it is concluded that they all occur by inner-sphere pathways.

Introduction

The transient 17-electron species $Rh(dmgH)_2PPh_3$[1] is formed from its parent dimer, $[Rh(dmgH)_2PPh_3]_2$, by irradiating into the dimer's principal visible absorption band[2] ($\lambda = 452$ nm, $\epsilon = 5 \times 10^4$ L mol^{-1} cm^{-1}). It has been established by X-ray diffraction[3] that this dimer consists of two monomeric halves linked by a rhodium–rhodium single bond.

The rhodium(II) radical $Rh(dmgH)_2PPh_3$ undergoes rapid dimerization,[4] re-forming the parent dimer. The photodissociation and recombination reactions are represented by eq 1.

$$[Rh(dmgH)_2PPh_3]_2 \xrightleftharpoons[k_D]{h\nu} 2Rh(dmgH)_2PPh_3 \qquad (1)$$

Alkyl halides react with the rhodium(II) radical by halogen atom abstraction,[5] as shown in eq 2. The analogous cobalt(II)

$$Rh(dmgH)_2PPh_3 + RX \rightarrow XRh(dmgH)_2PPh_3 + R^\bullet \qquad (2)$$

complexes, $Co(dmgH)_2L$, react similarly with alkyl halides[6] but show no tendency to dimerize.

The transient 17-electron species $Mn(CO)_5$ and $Re(CO)_5$ have also been shown[7] to undergo halogen atom transfer reactions with alkyl halides.

Another type of reaction in which a transfer of a halogen atom occurs is the inner-sphere reduction of $Co(NH_3)_5X^{2+}$ by species[8] such as Cr^{2+}, Eu^{2+}, and Fe^{2+}. No study has been reported in which one of the transient 17-electron species described here has reacted with a potential inner-sphere oxidant such as $Co(NH_3)_5X^{2+}$. In the present work we report the first such study, the oxidation of $Rh(dmgH)_2PPh_3$ by a series of cobalt(III) complexes.

Experimental Section

Reagents. $ClRh(dmgH)_2PPh_3$ was prepared by a literature method.[9] The rhodium dimer $[Rh(dmgH)_2PPh_3]_2$ was prepared from the chloro complex by borohydride reduction, yielding a hydridorhodoxime that decomposes to the dimer upon addition of hydrochloric acid, as described previously.[10] The cobalt(III) complexes were all previously prepared by standard methods. Halide salts were converted to perchlorate salts by dissolving them in dilute aqueous perchloric acid and precipitating with sodium perchlorate. The neutral complexes $ClCo(dmgH)_2PPh_3$ and $BrCo(dmgH)_2PPh_3$ were sufficiently soluble in the 95% ethanol solvent, as were the perchlorate salts $[Co(NH_3)_5Br](ClO_4)_2$ and $[Co(NH_3)_5N_3](ClO_4)_2$. All the other cobalt(III) compounds were converted to their triflate salts to increase their solubility in 95% ethanol. This was done by adding the perchlorate salt to the triflate form of Dowex 1-X8 anion-exchange resin. The resin was filtered off and the filtrate rotary evaporated to yield crystals of the triflate salt. The solubilities of these triflate salts in 95% ethanol ranged from ~2 mM for $[Co(NH_3)_5CN](CF_3SO_3)_2$ to >15 mM for $[Co(NH_3)_5H_2O](CF_3SO_3)_3$.

Table I. Rate Constants[a] for the Reaction of $Rh(dmgH)_2PPh_3$ with Cobalt(III) Complexes

Co^{III} complex	k/L mol^{-1} s^{-1}	Co^{III} complex	k/L mol^{-1} s^{-1}
$ClCo(dmgH)_2PPh_3$	1.3×10^8	$Co(NH_3)_5NCS^{2+}$	2.6×10^8
$BrCo(dmgH)_2PPh_3$	1.8×10^8	$Co(NH_3)_5Br^{2+}$	3.0×10^8
$Co(NH_3)_5F^{2+}$	2.9×10^6	$Co(NH_3)_5H_2O^{3+}$	$<7 \times 10^5$
$Co(NH_3)_5Cl^{2+}$	2.3×10^8	$Co(NH_3)_5CN^{2+}$	$<3 \times 10^6$
$Co(NH_3)_5N_3^{2+}$	2.6×10^8	$Co(NH_3)_6^{3+}$	$<1 \times 10^6$

[a] At 23 °C in 95% ethanol.

Kinetic Procedures. The kinetic experiments were carried out with a laser flash photolysis system closely modeled after one described in the literature.[11] The laser dye Coumarin 504, which gives an intensity maximum at 499 nm, was used. The kinetics relied on a single laser flash, and two-photon photochemistry was assumed to be unimportant. The kinetics of the reactions between $Rh(dmgH)_2PPh_3$ and the cobalt(III) complexes were monitored at 590 nm, an absorption maximum for the rhodium radical ($\epsilon \sim 2000$ L mol^{-1} s^{-1}).[5] The cobalt(III) concentrations were in the range 10^{-4}–10^{-2} mol L^{-1}. This was sufficient to ensure that the initial Co(III) concentration was much larger than the $\sim 10^{-5}$ M rhodium concentration generated by the laser pulse. This is consistent with the finding that the reaction follows pseudo-first-order kinetics. The solvent was 95% ethanol. Triphenylphosphine (4×10^{-4} M) was added in all kinetic experiments to suppress the dissociation of triphenylphosphine from $Rh(dmgH)_2PPh_3$.[5] Oxygen was removed from all solutions by purging with argon. Kinetic measurements were carried out at 23 (±1) °C.

Cobalt(II) Analysis. A solution of $[Rh(dmgH)_2PPh_3]_2$ and excess $Co(NH_3)_5NCS^{2+}$ in 95% ethanol was placed in a 1-cm cell. After 12 laser shots, the solution was poured out of the cell and diluted with water. Ammonium thiocyanate was added, followed by acetone, forming a 50% acetone solution, in which case any Co(II) is converted to $Co(NCS)_4^{2-}$. This solution was placed in a 5-cm cell and its visible spectrum measured.[12]

Results

The reactions of $Rh(dmgH)_2PPh_3$ with a series of cobalt(III) complexes were studied. An excess of the cobalt(III) complexes was added to a solution of the dimer, which was then pulsed with a laser beam. The decay in absorbance at 590 nm was monitored; it followed pseudo-first-order kinetics. First-order rate constants were obtained by a nonlinear-least-squares method.[13] These were plotted against the concentration of the cobalt(III) complex, the slope of this plot giving the second-order rate constant. The plots obtained for each cobalt(III) complex are shown in Figure 1. The

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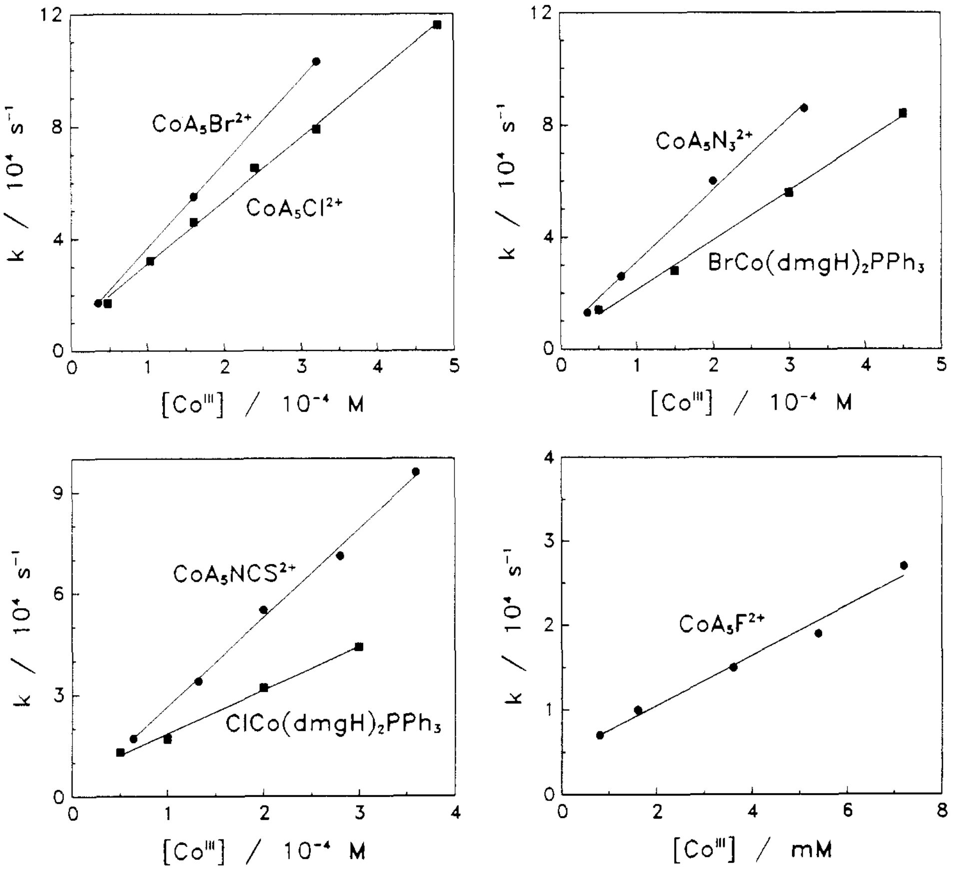

Figure 1. Reaction of $Rh(dmgH)_2PPh_3$ with cobalt(III) complexes, illustrated by plots of observed pseudo-first-order rate constants versus concentrations of cobalt(III) complexes ($[Rh(dmgH)_2PPh_3]_0 \sim 10^{-5}$ M; solvent = 95% ethanol; λ = 590 nm; $[PPh_3] = 4 \times 10^{-4}$ M).

plots all give small intercepts; these are due to the competing dimerization of $Rh(dmgH)_2PPh_3$. The values of the second-order rate constants obtained are given in Table I. The observed rate law is given in eq 3. For three of the compounds studied, Co-

$$-d[Rh(dmgH)_2PPh_3]/dt = 2k_D[Rh(dmgH)_2PPh_3]^2 + k[Rh(dmgH)_2PPh_3][Co^{III}] \quad (3)$$

$(NH_3)_5H_2O^{3+}$, $Co(NH_3)_5CN^{2+}$, and $Co(NH_3)_6^{3+}$, the reactions with $Rh(dmgH)_2PPh_3$ were too slow to obtain a rate constant. In these cases only the dimerization of $Rh(dmgH)_2PPh_3$ was observed. Upper limits for the second-order rate constants of these complexes were estimated. These values are given in Table I. The different upper limits quoted for each of these complexes reflect differences in the concentrations as limited by their solubilities.

The identity of the rhodium product formed by the reaction of $Rh(dmgH)_2PPh_3$ with $Co(NH_3)_5Cl^{2+}$ was investigated. A solution containing $[Rh(dmgH)_2PPh_3]_2$ and $Co(NH_3)_5Cl^{2+}$ was repeatedly subject to successive laser flashes. The UV/visible spectrum of the product solution, corrected for the spectrum of excess $Co(NH_3)_5Cl^{2+}$, resulted in a spectrum with a peak at 266 nm. A separately prepared sample of $ClRh(dmgH)_2PPh_3$ has a peak at 272 nm.

The identity of the cobalt product formed by the reaction of $Rh(dmgH)_2PPh_3$ with $Co(NH_3)_5NCS^{2+}$ was investigated. A cobalt(II) analysis,[12] carried out on a solution initially containing 2.2×10^{-5} M $[Rh(dmgH)_2PPh_3]_2$ and 8×10^{-5} M $Co(NH_3)_5NCS^{2+}$, yielded 2.5×10^{-5} M Co^{2+}. This is approximately 60% of the maximum expected yield; the difference is unaccounted for, but it may simply reflect the uncertainty of the analytical method at such very low Co(II) concentrations. We presume by analogy that the rhodium product is $Rh(dmgH)_2(SCN)(PPh_3)$ formed by an inner-sphere mechanism, although this was not checked as this is apparently an unknown compound.

Discussion

The measured second-order rate constants for the reaction of $Rh(dmgH)_2PPh_3$ with the cobalt(III) complexes range from <7 $\times 10^5$ L mol^{-1} s^{-1} for $Co(NH_3)_5H_2O^{3+}$ to 3.0×10^8 L mol^{-1} s^{-1} for $Co(NH_3)_5Br^{2+}$. For the halides, the "normal" reactivity order[14] is observed, i.e., $Br^- > Cl^- > F^-$. The k_{Br}/k_{Cl} ratios are almost identical for $XCo(dmgH)_2PPh_3$ ($k_{Br}/k_{Cl} = 1.4$) and $Co(NH_3)_5X^{2+}$ ($k_{Br}/k_{Cl} = 1.3$).

Table II. Relative Rate Constants for the Reactions of $Ru(NH_3)_6^{2+}$ and $Rh(dmgH)_2PPh_3$ with Cobalt(III) Complexes

	$k_{Co(NH_3)_5X}/k_{Co(NH_3)_5Br}$	
Co^{III} complex	$Ru(NH_3)_6^{2+}$	$Rh(dmgH)_2PPh_3$
$Co(NH_3)_5Cl^{2+}$	0.16[a]	0.77
$Co(NH_3)_5N_3^{2+}$	8×10^{-4}[a]	0.87

[a] $k_{Co(NH_3)_5Br} = 1.6 \times 10^3$ L mol^{-1} s^{-1} in aqueous solution.[15]

All the cobalt(III) complexes studied, with the exception of $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_6^{3+}$, can conceivably react by an inner-sphere or an outer-sphere pathway, as shown in eq 4 and 5. A good example of an outer-sphere reaction of this type is

$$M + XCo \rightarrow [M\text{---}X\text{---}Co] \rightarrow MX + Co \quad (4)$$

$$M + XCo \rightarrow [M^+ + XCo^-] \rightarrow M^+ + X^- + Co \quad (5)$$

that between $Ru(NH_3)_6^{2+}$ and $Co(NH_3)_5X^{2+}$. $Ru(NH_3)_6^{2+}$ is substitution inert, preventing a bridging ligand from entering the inner coordination sphere. This reaction should therefore obey the Marcus theory, with the rate constant being a function of the driving force for the reaction and the self-exchange rate constants of the reactants. If a pair of cobalt(III) complexes is considered, the ratio of the two rate constants will be a function of the reduction potentials and self-exchange rate constants for the cobalt(III) complexes but will not depend on the reductant. Thus, the present results, with $Rh(dmgH)_2PPh_3$ as reductant, can be compared directly with the $Ru(NH_3)_6^{2+}$ results,[15] as shown in Table II. For $Rh(dmgH)_2PPh_3$, the ratio $k_{Co(NH_3)_5Cl}/k_{Co(NH_3)_5Br}$

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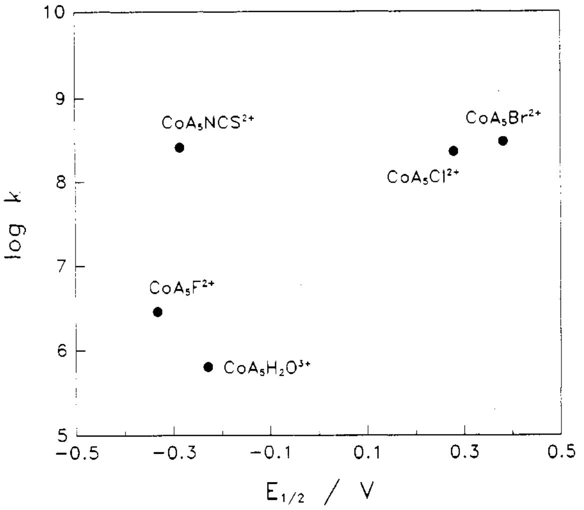

Figure 2. Reaction of $Rh(dmgH)_2PPh_3$ with cobalt(III) complexes, illustrated by plot of the logarithms of the measured second-order rate constants versus half-wave reduction potentials of cobalt(III) complexes.

is 5 times greater than it is for $Ru(NH_3)_6^{2+}$. The ratio $k_{Co(NH_3)_5N_3}/k_{Co(NH_3)_5Br}$ is 10^3 times greater for $Rh(dmgH)_2PPh_3$ than for $Ru(NH_3)_6^{2+}$. This is clearly a significant deviation from the Marcus theory, suggesting that the $Rh(dmgH)_2PPh_3$ reaction is not outer-sphere.

In a previous study[5] of the reaction of $Rh(dmgH)_2PPh_3$ with alkyl halides, an approximately linear correlation was observed between the second-order rate constant and the half-wave reduction potentials of the alkyl halides, which we take as an approximate measure of $E°$. Half-wave reduction potentials are available[16] for some of the cobalt(III) complexes used in the present study, enabling a plot to be made of the second-order rate constant versus $E_{1/2}$. This plot is shown in Figure 2. No correlation is observed. We take this as further evidence against an outer-sphere mechanism. Some caution is in order, however, in that true reduction potentials (for alkyl halides and for cobalt(III) complexes) are not available. The use of $E_{1/2}$ values for irreversible couples is risky, in that voltages associated with irreversible electrode processes cannot be directly taken as $E°$ for a redox couple.

The UV/visible spectrum of the product of the reaction of $Rh(dmgH)_2PPh_3$ with $Co(NH_3)_5Cl^{2+}$ suggests that the chlororhodium complex, $ClRh(dmgH)_2PPh_3$, is the only significant product. As rhodium(III) complexes are substitution inert, this demonstrates that the reaction is inner-sphere. An outer-sphere reaction would yield an aquo–rhodium product.

The observed reactivity order for $Co(NH_3)_5X^{2+}$, $Br^- > Cl^- > F^-$, can be rationalized in terms of a reaction between a soft metal center (Rh^{II}) and a hard metal center (Co^{III}). If the reaction occurs by an inner-sphere mechanism with a rate-determining electron-transfer step, the second-order rate constant is given by the product of the equilibrium constant for the formation of the precursor complex, K_{eq}, and the rate constant for intramolecular electron transfer in the precursor complex, k_{et}. Since a hard metal forms a more stable fluoride complex and a soft metal forms a more stable bromide complex, in the present case one would expect K_{eq} to decrease in the order $Br^- > Cl^- > F^-$. The overall reactivity order is also determined by k_{et}. Since Br^- has a higher electron permeability than F^-, one would also predict a decrease in k_{et} in the order $Br^- > Cl^- > F^-$. The two effects combined to give the normal reactivity order.

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Reactions of Sulfur Dioxide with Photochemically Generated Polypyridyl Complexes of Chromium(II). Calculation of the $SO_2/SO_2^{\bullet -}$ Self-Exchange Rate Constant[1]

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Three reactions occur when $Cr(NN)_3^{3+}$ ions (NN = bpy, phen, and substituted analogues) are subjected to visible light from a laser pulse in solutions containing SO_2 in 1.0 M H_2SO_4. The quenching reaction produces $Cr(NN)_3^{2+}$ quantitatively. The $Cr(NN)_3^{2+}$ so produced undergoes back electron transfer, but in the presence of millimolar concentrations of SO_2 the predominant reaction is electron transfer between $Cr(NN)_3^{2+}$ and SO_2, yielding the transient $SO_2^{\bullet -}$. The rate constants for both back electron transfer and SO_2 reduction are correlated by the Marcus cross-relation. The calculated value of the $SO_2/SO_2^{\bullet -}$ self-exchange rate constant covers the range (1–18) × 10^4 L mol^{-1} s^{-1} at 25 °C in 1.0 M H_2SO_4.

Introduction

Self-exchange reactions between small molecules and their one-electron-reduced partners continue to be of interest. In a recent study involving the $O_2/O_2^{\bullet -}$ pair, it was noted that the reactions fell into two distinct categories, depending on the direction in which kinetic data were determined.[2] Consider the transformation $O_2 + D \rightleftarrows O_2^{\bullet -} + D^+$. The autoxidation reactions yielded kinetic data that were correlated by the Marcus cross-relation[3-6] and gave consistent values for k_{11}, the $O_2/O_2^{\bullet -}$ self-exchange rate constant. On the other hand, widely scattered values of k_{11} were obtained when data for the reductions by the superoxide radical ion were examined.[2]

The $SO_2/SO_2^{\bullet -}$ couple has been examined only in reactions starting with $SO_2^{\bullet -}$.[7] The reported self-exchange rate constants, k_{ex}, span a large range of values, from 10^2 to 10^9 M^{-1} s^{-1}.[8-11] The values significantly different from ~10^3 M^{-1} s^{-1} have recently been discarded as unreliable,[11] either because there is uncertainty in the parameters needed in the calculations or because the mechanism has not been established with certainty. This left no reliable estimate of k_{ex} for the $SO_2/SO_2^{\bullet -}$ couple based on oxidations by

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