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Superoxide Complexes of Tetrakis(μ-2-anilinopyridinato)dirhodium(II,II) and -dirhodium(II,III): The One-Electron Catalytic Reduction of Dioxygen

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Received June 14, 1988

The tetrakis(μ-2-anilinopyridinato)dirhodium(II,III) cation, $[(ap)_4Rh^{II}Rh^{III}]^+$, has four possible geometric isomers. The isomer with four pyridyl nitrogens bound to one rhodium ion and four anilino nitrogens bound to the second rhodium ion was investigated with respect to its electrochemical and oxygen binding properties. The $[(ap)_4Rh^{II}Rh^{III}]^+$ complex can be reversibly reduced by one electron to form $(ap)_4Rh^{II}_2$. This reaction occurs at -0.31 V vs SCE in CH_2Cl_2 when the associated anion on $[(ap)_4Rh^{II}Rh^{III}]^+$ is ClO_4^-. The electrogenerated $(ap)_4Rh^{II}_2$ can rapidly bind molecular oxygen to form $(ap)_4Rh^{II}Rh^{III}(O_2^-)$, and the reduction of this compound occurs at $E_{1/2} = -0.48$ V vs SCE to generate $[(ap)_4Rh^{II}_2(O_2^-)]^-$. The latter complex has a rhombic ESR signal with $g_1 = 2.094$, $g_2 = 2.026$, and $g_3 = 1.998$. The electrochemically generated $[(ap)_4Rh^{II}_2(O_2^-)]^-$ will react with CH_2Cl_2, leading to CH_2O, Cl^-, and the original $(ap)_4Rh^{II}_2$ complex, which then reconverts to $(ap)_4Rh^{II}Rh^{III}(O_2^-)$ under an O_2 atmosphere. The rate constant for the overall reaction of $[(ap)_4Rh^{II}_2(O_2^-)]^-$ with CH_2Cl_2 is 0.2 s^{-1} at 25 °C, and this value is independent of the partial pressure of dioxygen. The presence of an O_2^- scavenger significantly increases the electrocatalytic current. The catalytic properties of the complex are strongly influenced by axial ligation with the solvent, and no reactions with O_2 occur in dimethylformamide or acetonitrile.

Introduction

Extensive effort has gone into finding efficient catalysts that can promote the reaction of dioxygen with oxidizable substrates.[1,2] Biological catalysts are effective in activation and transport of dioxygen, and in this regard, metalloporphyrin catalysts have received much attention.[3-9] However, there are few additional examples of transition-metal complexes that have the desired properties and reactivity to be utilized in the catalytic activation of dioxygen.

Activation of molecular oxygen by transition-metal complexes can occur via a one-electron-transfer process, a two-electron-transfer process, or a four-electron-transfer process, which will generate the superoxide ion, peroxide ion, or oxide ion, in aprotic media.[10-18] The superoxide ion is reactive toward some organic substrates either by nucleophilic substitution or by direct oxidation. It has been used for the degradation of chloroalkanes, chloroalkenes, and polychloro aromatic hydrocarbons.[19-21] Solutions containing O_2^- can be prepared in aprotic solvents by electrochemical methods[22,23] or by solubilizing KO_2 with 18-crown-6-ether.[24] However, there is still a need to find convenient and inexpensive pathways to continuously generate O_2^-.[25,26]

A catalytic cycle involving manganese porphyrins for the reduction of dioxygen has been reported by Murray.[8,9] Mixtures of the porphyrin and benzoic anhydride led to a reduction of dioxygen at a controlled potential of -0.40 V vs SCE. This process involved reduction by more than two electrons and heterolysis of the O-O bond by benzoic anhydride. However, the Mn porphyrin complex did not show catalytic behavior in the absence of benzoic anhydride.

This paper reports the reactivity of $(ap)_4Rh^{II}_2$ (ap = 2-anilinopyridinate ion) with dioxygen. The synthesis, structure, and ESR properties of two geometric isomers of the tetrakis(μ-2-anilinopyridinato)dirhodium complex have been recently reported.[27] The isomer investigated in this study has the four pyridyl nitrogens of the anilinopyridine ligands bound to one rhodium ion and the four anilino nitrogens of the bridging ligands bound to the second rhodium ion. The complex can be reduced in CH_2Cl_2 and in the presence of molecular oxygen will result in the formation of $(ap)_4Rh^{II}Rh^{III}(O_2^-)$. Further reduction at -0.48 V gives the superoxide complex, $[(ap)_4Rh^{II}_2(O_2^-)]^-$. The complexes are characterized as to their spectroscopic properties and reactivity and are the first examples of dirhodium compounds that can catalytically activate molecular oxygen.

Experimental Section

Synthesis of the Rhodium Complexes. $(ap)_4Rh_2Cl$ was synthesized by heating 300 mg of $Rh_2(OAc)_4$ in 5 g of 2-anilinopyridine under vacuum at 130 °C for 24 h. Unreacted 2-anilinopyridine was removed by sublimation and the solid mixture then dissolved in a CH_2Cl_2 solution containing CCl_4. Repeated purification on a silica gel column with 5% CH_3OH in CH_2Cl_2 gave a pure product in 40% yield.

$(ap)_4Rh_2ClO_4$ was generated by reducing 50 mg of $(ap)_4Rh_2Cl$ in CH_2Cl_2, 0.05 M TBAP at -0.65 V under a CO atmosphere. The pinkish brown $(ap)_4Rh_2(CO)$ product precipitates from solution. This precipitate was filtered and washed with cold CH_2Cl_2. Carbon monoxide was removed, and $(ap)_4Rh_2ClO_4$ was generated by oxidizing the CO adduct at +0.2 V in CH_2Cl_2, 0.1 M TBAP under an argon atmosphere.

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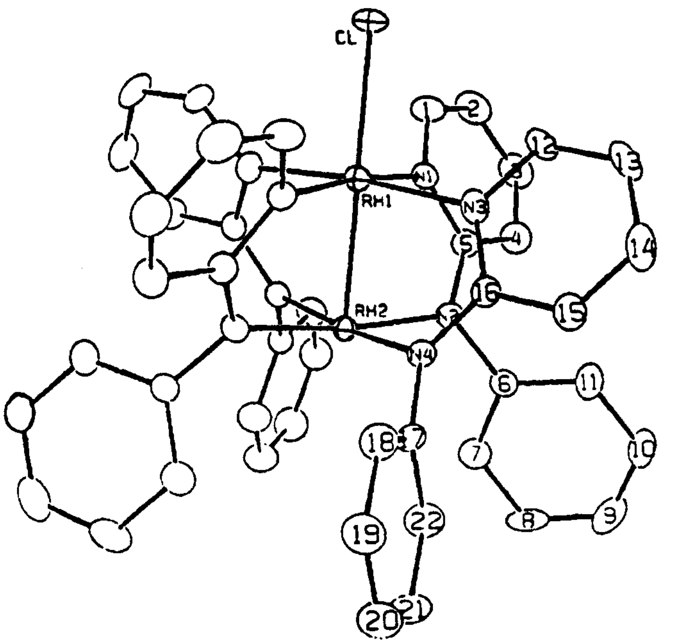


Figure 1. Molecular structure of $(ap)_4Rh_2Cl$.

Solvents and Reagents. All reagents for synthesis were used as received. Spectroscopic grade CH_2Cl_2 was purified by distillation from CaH_2 under N_2. Dimethylformamide (DMF) was vacuum-distilled from 4-Å activated molecular sieves, and tetrahydrofuran (THF) was distilled from CaH_2 followed by distillation over Na/benzophenone under N_2. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP), was twice recrystallized from ethanol and dried in a vacuum oven at 40 °C. Ultrahigh-purity O_2 (Big Three, Inc.) with a maximum of 3 ppm of H_2O was used.

Instrumentation. A three-electrode cell was used for electrochemical experiments. A platinum-button electrode with surface area of 0.19 mm^2 was used for cyclic voltammetry, and a platinum-gauze electrode was used for controlled-potential electrolysis. The surface area of the rotating Pt-disk electrode was 0.168 cm^2. Potentials are referenced to a saturated calomel reference electrode (SCE), which was separated from the bulk solution by a fritted-glass disk.

An IBM 225 voltammetric analyzer was used to record the cyclic voltammograms. Rotating-disk voltammograms were obtained with a Pine Model RE4 potentiostat coupled with a MSR high-performance rotator. An EG&G PAR Model 173 potentiostat/galvanostat coupled with a Houston 2000 X-Y recorder was used to perform controlled-potential electrolysis. The partial pressure of dioxygen was varied by using a Matheson Dyna-Blender Model 8250 flow controller.

Results and Discussion

The molecular structure of $(ap)_4Rh^{II}Rh^{III}Cl$ is given in Figure 1. This complex is the most polar of the four possible geometric isomers that could be formed by the 2-anilinopyridinate bridging ligand. Each of the rhodium ions is in a different equatorial ligand environment, and in addition only one axial ligand bond is formed.[27] This is true for either of the two formal oxidation states, $(ap)_4Rh^{II}_2$ or $[(ap)_4Rh^{II}Rh^{III}]^+$. The chloride ion is bound to the rhodium with four pyridyl nitrogen bonds, and this rhodium is probably the preferred binding site of dioxygen in the complex to be discussed. The ESR spectrum of $(ap)_4Rh^{II}Rh^{III}Cl$ is unique among all other dirhodium complexes studied in that the odd electron is localized on one rhodium ion, showing the complex to contain a true Rh(II)–Rh(III) dimer unit.[27] The HOMO of $(ap)_4Rh^{II}_2(L)$ (where L = an anionic or neutral ligand) should also be highly polarized, giving the complex properties somewhat like those of a Rh(I)–Rh(III) compound. This electronic effect coupled with the steric constraints imposed on the molecule by the four phenyl substituents is the reason that the complex forms only monoadducts.

$(ap)_4Rh_2Cl$ undergoes a single reversible reduction at $E_{1/2}$ = −0.38 V and a single reversible oxidation at $E_{1/2}$ = +0.52 V in CH_2Cl_2, 0.1 M TBAP. The bound Cl^- ion on $(ap)_4Rh_2Cl$ can be replaced by ClO_4^- to give $(ap)_4Rh_2ClO_4$ (as described in the Experimental Section), and this leads to a 70-mV shift in the reduction potential and a 10-mV shift in the oxidation potential. This is illustrated in Figure 2a for the reduction and oxidation of $(ap)_4Rh_2ClO_4$ in CH_2Cl_2 containing 0.1 M TBAP. $(ap)_4Rh^{II}_2$ is formed upon reduction at $E_{1/2}$ = −0.31 V (process 2), while $[(ap)_4Rh^{III}_2]^{2+}$ is generated upon oxidation at $E_{1/2}$ = 0.53 V (process 1).[27]

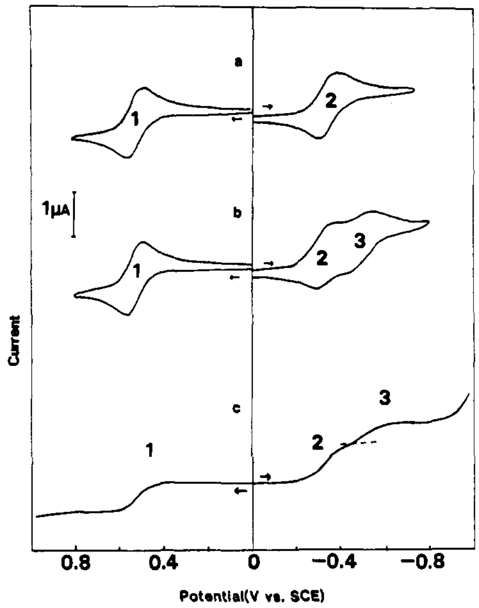


Figure 2. Cyclic voltammograms of 1.0 × 10^{-3} M $(ap)_4Rh_2ClO_4$ in CH_2Cl_2, 0.1 M TBAP at a scan rate of 0.10 V/s (a) under nitrogen and (b) under oxygen. (c) Linear-sweep voltammogram of the same solution at a rotating disk electrode. Scan rate = 0.01 V/s; rotation rate = 500 rpm.

The potentials for processes 1 and 2 do not change when oxygen is bubbled through the solution, but under these conditions, a new quasi-reversible reduction (process 3) appears at $E_{1/2}$ = −0.48 V. The ratio of cathodic peak currents for process 3 to those for process 2 decreases with either an increase in scan rate or a decrease in temperature. This clearly indicates a reaction of electrogenerated $(ap)_4Rh^{II}_2$ with dioxygen.

The electrochemistry of $(ap)_4Rh_2ClO_4$ at a rotating Pt-disk electrode in the presence of O_2 is shown in Figure 2c and gives results similar to those obtained by cyclic voltammetry. In the absence of dioxygen the complex undergoes a one-electron reduction and a one-electron oxidation. However, in the presence of dioxygen there are two one-electron reductions, the latter of which occurs at $E_{1/2}$ = −0.48 V. There is no interference from the direct reduction of O_2, which occurs at E_p = −1.0 V in CH_2Cl_2, 0.1 M TBAP at a scan rate of 0.10 V/s.

The ratio of the limiting current for wave 3 to that for wave 2 by rotating-disk voltammetry is 0.72 at 500 rpm, and the data in Figure 2 thus suggest the following sequence of reactions:

$$[(ap)_4Rh^{II}Rh^{III}]^+ + e^- \rightleftarrows (ap)_4Rh^{II}_2 \qquad (1)$$

$$(ap)_4Rh^{II}_2 + O_2 \rightleftarrows (ap)_4Rh^{II}Rh^{III}(O_2^-) \qquad (2)$$

$$(ap)_4Rh^{II}Rh^{III}(O_2^-) + e^- \rightleftarrows [(ap)_4Rh^{II}_2(O_2^-)]^- \qquad (3)$$

The ultimate product of the first reduction is a dirhodium dioxygen adduct and is assigned as the dirhodium-superoxide complex, $(ap)_4Rh^{II}Rh^{III}(O_2^-)$, on the basis of its UV-visible spectrum, which clearly indicates the presence of a $Rh^{II}Rh^{III}$ center. The first reduction product has absorption peaks at 900 nm (ϵ = 3.7 × 10^3) and 1600 nm (ϵ = 2.8 × 10^3), and the overall spectrum is similar to that of the initial $(ap)_4Rh_2ClO_4$ complex, which has peaks at 890 nm (ϵ = 3.3 × 10^3) and 1540 nm (ϵ = 2.7 × 10^3). In contrast, the spectrum of the first reduction product under an Ar atmosphere (reaction 2, Figure 2a) does not have absorption peaks above 800 nm.

The formation of $[(ap)_4Rh^{II}_2(O_2^-)]^-$ as the product of reaction 3 is demonstrated by the ESR spectrum of a frozen-glass solution

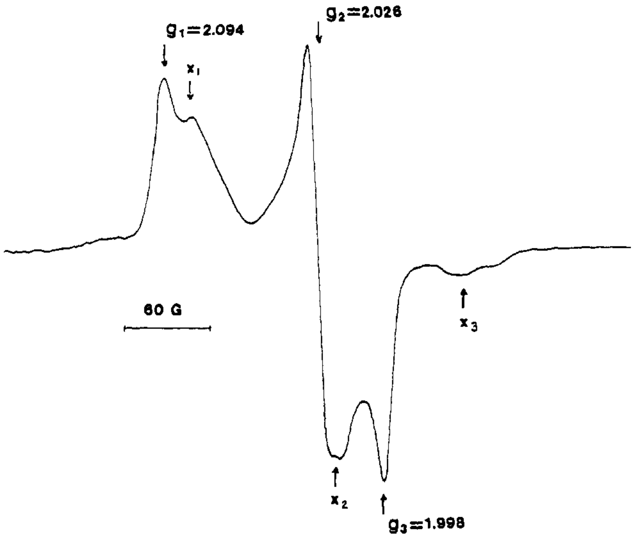


Figure 3. ESR spectrum of singly reduced $(ap)_4Rh_2^{II,III}(O_2^-)$ at 123K in CH_2Cl_2, 0.1 M TBAP.

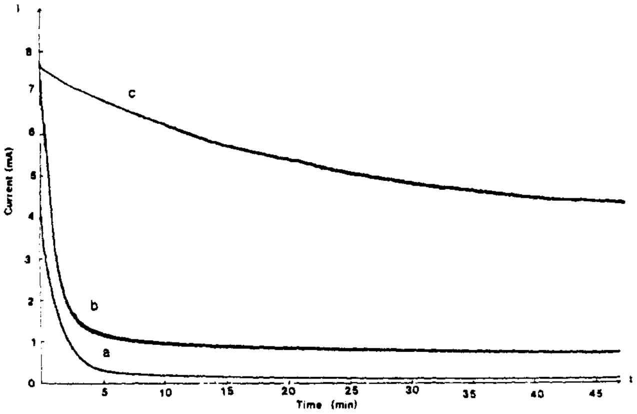
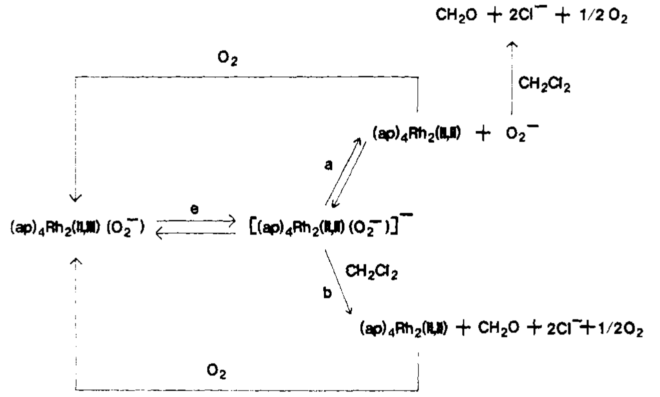


Figure 4. Current–time curves for the controlled-potential reduction of 5.1×10^{-4} M $(ap)_4Rh^{II}Rh^{III}(O_2^-)$ in CH_2Cl_2, 0.1 M TBAP at −0.60 V. Curve a was obtained under N_2, curve b under O_2, and curve c under the same solution conditions as curve b but with added 0.1 M benzoic anhydride.

Scheme I. Reaction Mechanism of $(ap)_4Rh_2(O_2^-)$ under O_2 in CH_2Cl_2



taken after bulk controlled-potential reduction of $(ap)_4Rh^{II}Rh^{III}(O_2^-)$ at −0.60 V in CH_2Cl_2. This ESR spectrum is shown in Figure 3 and has a rhombic signal with $g_1 = 2.094$, $g_2 = 2.026$, and $g_3 = 1.998$. There are also three small signals (marked X) that appear after 30 min or more of electrolysis. The species responsible for these signals has not been identified. However, the g values of X_1 and X_3 correspond to $g_\perp$ and $g_\parallel$ for $(ap)_4Rh^{II}Rh^{III}Cl$. In addition, X_3 is split into a doublet as is $g_\parallel$ for the latter complex. The g value for X_2 is in the region expected for a free radical, which could be generated in the reaction of O_2^- with CH_2Cl_2.

There is no splitting of the O_2^- signal by the nuclear spin of rhodium ($S = {}^1/_2$), and the ESR spectrum in Figure 3 is thus consistent with that of a diamagnetic Rh^{II}_2 unit containing axially bound superoxide. A monomeric rhodium dioxygen complex $(TPP)Rh(O_2)$, where TPP is the dianion of tetraphenylporphyrin, shows a similar ESR spectrum with $g_1 = 2.087$, $g_2 = 2.026$, and $g_3 = 1.991$[28,29] and has been described as a Rh^{III}–O_2^- species.[29]

Controlled-potential electrolysis of $(ap)_4Rh^{II}Rh^{III}(O_2^-)$ was carried out in CH_2Cl_2 under N_2 at −0.60 V, and the integrated current–time curve gave a total of 1.0 ± 0.1 electrons transferred as the current decreased to zero. This is shown in curve a of Figure 4. However, the residual current was larger when electrolysis of the same solution was carried out under an O_2 atmosphere (see curve b, Figure 4). Under these conditions, the steady-state current did not decay to zero at all times up to 5 h of electrolysis, thus indicating that no significant decomposition of the complex occurred. The final steady-state current in curve b, Figure 4, also did not vary with changes in the partial pressure of oxygen between 160 and 760 mmHg, suggesting that the reaction between $(ap)_4Rh^{II}_2$ and O_2 is pseudo first order with respect to the dirhodium complex. Finally, a turnover number of 4 was calculated when the bulk electrolysis of $(ap)_4Rh^{II}Rh^{III}(O_2^-)$ was stopped after 1 h.

The above electrochemical results support a catalytic reduction of dioxygen in the sense that the original irreversible reduction of O_2 is shifted from $E_p = -1.0$ V in CH_2Cl_2 containing 0.1 M TBAP to $E_{1/2} = -0.48$ V in the same solution containing $[(ap)_4Rh^{II}Rh^{III}]^+$. The reduction of $(ap)_4Rh^{II}Rh^{III}(O_2^-)$ occurs at the $Rh^{II}Rh^{III}$ center and results in the overall EC catalytic process shown in Scheme I.

Route a in Scheme I involves an association–dissociation mechanism. $[(ap)_4Rh^{II}_2(O_2^-)]^-$ undergoes dissociation of O_2^- to give $(ap)_4Rh^{II}_2$, which then reacts with molecular O_2 to regenerate $(ap)_4Rh^{II}Rh^{III}(O_2^-)$. The superoxide ion is known to react with CH_2Cl_2 and gives as a final products CH_2O, Cl^-, and O_2.[19] This reaction most likely occurs in the present system since no free O_2^- was detected by ESR in CH_2Cl_2. The second process in Scheme I (route b) involves the direct attack of $[(ap)_4Rh^{II}_2(O_2^-)]^-$ by a CH_2Cl_2 solvent molecule, and would also regenerate $(ap)_4Rh^{II}Rh^{III}(O_2^-)$ under an O_2 atmosphere. Both processes a and b would provide the necessary thermodynamic driving force to shift the reduction potential of O_2 by about 0.5 V. Thus, the data obtained can be used to explain either process a or process b, and neither of the two possible routes can be eliminated. However, if route b occurs, the rate of the reaction of $[(ap)_4Rh^{II}_2(O_2^-)]^-$ with CH_2Cl_2 must be slow, since an ESR spectrum of the superoxide complex is easily obtained in this solvent.

The overall rate constant for reaction of the Rh^{II}_2 complex with O_2 was determined by monitoring the reduction currents after complete conversion of $(ap)_4Rh^{II}Rh^{III}(O_2^-)$ to $[(ap)_4Rh^{II}_2(O_2^-)]^-$ by bulk controlled-potential electrolysis at −0.60 V. For this type of catalytic process, the ratio of reduction current in the presence of oxygen, i_{cat}, to the current in the absence of oxygen, i_0, varies linearly with $t^{1/2}$ for $(kt)^{1/2} > 2$, as shown in eq 4.[30]

$$i_{cat}/i_0 = (kt)^{1/2}[\pi^{1/2}\,\mathrm{erf}((kt)^{1/2}) + (\exp(-kt))/(kt)^{1/2}] \qquad (4)$$

A plot of i_{cat}/i_0 vs $t_{1/2}$ using data of the type shown in Figure 4 was contructed and gave an estimated $k = 0.2\ s^{-1}$ for the overall reaction shown in Scheme I. The mass-transfer constant was eliminated by assuming that the electrode reduction process is diffusion controlled and that the regeneration of $(ap)_4Rh^{II}_2$ is the rate-determining step. All experiments in Figure 4 were carried out under identical conditions (stirring rate, electrode position,

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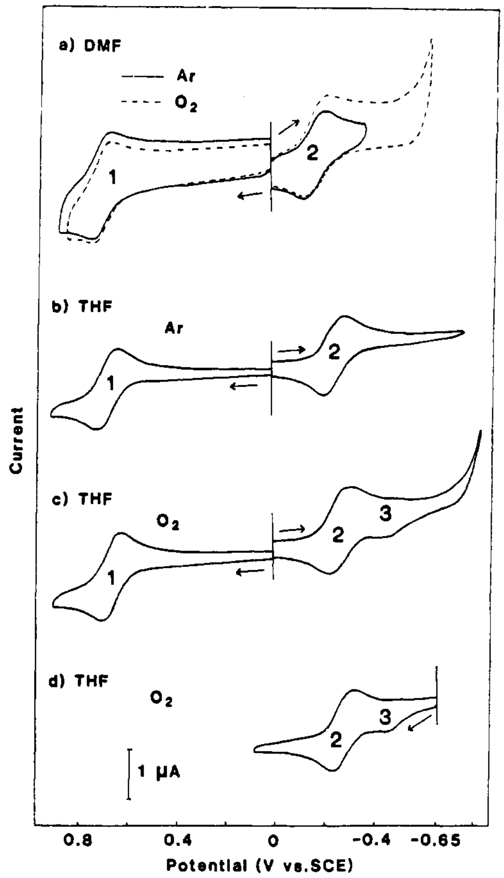

Figure 5. Cyclic voltammograms of $(ap)_4Rh_2ClO_4$: (a) in DMF, 0.1 M TBAP under Ar (—) and O_2 (---); (b) in THF, 0.1 M TBAP under Ar; (c) in THF, 0.1 M TBAP under O_2; (d) in THF, 0.1 M TBAP under O_2 but with initial potential scan started at −0.65 V.

electrode area, etc.). This was done by switching the gas source from O_2 to Ar or vice versa without moving the electrochemical cell setup.

The presence of an O_2^- scavenger facilitates O_2^- dissociation from $[(ap)_4Rh^{II}_2(O_2^-)]^-$ and results in a higher steady-state current for the reduction of $(ap)_4Rh^{II}Rh^{III}(O_2^-)$. The steady-state current for the catalytic reduction of oxygen increased from 0.8 to 4.0 mA when a solution containing the complex and 0.1 M benzoic anhydride was reduced at −0.60 V. This is illustrated by curve c, Figure 4. The current only decreased when the benzoic anhydride was depleted after 3 h of bulk electrolysis. A turnover number of 26 was found from integration of the current–time curve after 1 h of electrolysis assuming 100% current efficiency. The nature of the reaction between benzoic anhydride and $[(ap)_4Rh^{II}_2(O_2^-)]^-$ is not clear at this time.

The binding of O_2 to the dirhodium species is strongly influenced by the axial coordination environment. Figure 5 shows the cyclic voltammograms of $(ap)_4Rh_2ClO_4$ in DMF and THF containing 0.1 M TBAP under an O_2 or Ar atmosphere. The reactions of $(ap)_4Rh_2ClO_4$ under Ar shift from $E_{1/2} = -0.31$ and +0.53 V in CH_2Cl_2 to $E_{1/2} = -0.25$ and +0.65 V in DMF. This indicates a coordination of DMF to $(ap)_4Rh_2ClO_4$. Cyclic voltammograms of the complex under an O_2 atmosphere do not show a wave corresponding to oxygen activation. This same phenomenon is also observed in the potentially coordinating solvent CH_3CN. When THF is used as solvent, the redox potentials of $(ap)_4Rh_2ClO_4$ are located at $E_{1/2} = -0.23$ and +0.67 V, thus indicating a weak binding of THF to $(ap)_4Rh_2ClO_4$. The redox couple for the dirhodium oxygen adduct is clearly shown when O_2 is bubbled through the solution (see wave 3, Figure 5c,d). In this case, the cathodic wave is much smaller than the corresponding anodic wave, which suggests the reaction of $(ap)_4Rh^{II}_2$ with O_2 is a slower process in this solvent than that in CH_2Cl_2. A similar phenomenon can also be observed in the weakly coordinating solvent CH_3NO_2. These results show that O_2 and solvent molecules compete for the axial coordination site of $(ap)_4Rh^{II}_2$, and if the solvent binding constant is too large, no reduction of O_2 is observed.

In summary, this paper presents the properties of dioxygen complexes of the form $[(ap)_4Rh^{II}_2(O_2^-)]^-$ and $(ap)_4Rh^{II}Rh^{III}(O_2^-)$. The ESR spectrum of $[(ap)_4Rh^{II}_2(O_2^-)]^-$ and the UV–vis spectrum of $(ap)_4Rh^{II}Rh^{III}(O_2^-)$ are consistent with both compounds being superoxide complexes. This is an unusual situation where the oxidation state of the same metal–ligand unit is changed while dioxygen remains bound as a superoxide ion. Finally, this work presents the first example of a dinuclear rhodium(II) complex that can catalytically activate dioxygen through a one-electron-reduction process.

Acknowledgment. The support of the Robert A. Welch Foundation (J.L.B., Grant No. E-918; K.M.K., Grant No. E-680) is gratefully acknowledged.