2 - 아닐리노 피리딘을 배위자로 하는 이핵 로듐착물의 두 산소첨가 생성물에 대한 합성 및 전기화학적 성질

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Synthesis, ESR and Electrochemical Characterization of Dioxygen Binding to Dirhodium Complexes with 2-anilinopyridinato Bridging Ligand

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요 약. 두 개의 아닐린계 질소와 두 개의 피리딘계 질소가 각각의 로듐이온에 트란스형으로 결합된 $Rh_2(ap)_4$(2,2-trans) 이성질체는 -0.40 V vs SCE에서 더 옥시젼의 한 전자를 환원시킬 수 있음을 보여주고 있다. 123 K에서의 ESR 스펙트럼에 의하면 한 로듐이온에 산소 1분자가 측쇄 결합하여 $[Rh_2(ap)_4(O_2)]^-$이온을 형성하고, 착물은 Rh_2^{II} 산화수를 가짐을 알 수 있다. 이 착물은 시안화메틸/염화메틸렌 혼합용액에서 Rh-O_2^-결합의 분열없이 $[Rh_2(ap)_4(O_2)(CH_3CN)]^-$을 형성한다. -0.25, 0.55 V 에서 산화되었을 때 $[Rh_2(ap)_4(O_2)]^-$은 $Rh_2(ap)_4(O_2)$와 $[Rh_2(ap)_4(O_2)]^+$을 형성하기 위하여 두 단계의 한 전자 산화과정이 일어난다. 두 화학종은 모두 초산소가 측쇄 결합되어 있지만, 전자는 $Rh^{II}Rh^{III}$, 후자는 Rh_2^{III}의 산화수를 갖는다. 반면에, ESR 스펙트럼과 CH_3CN 부가 연구에서 보면 후자 착물이 로듐이온에 위치한 부대전자와 함께 $[Rh^{II}Rh^{III}(ap)_4(O_2)]^+$로 기술되고 그 착물은 측쇄 배위결합된 산소분자를 가지고 있음을 보여주고 있다. 또한 전기화학적, ESR 연구는 더 옥시젼의 활동도가 전기화학적 산화환원전위와 관계 있음을 보여주고 있다.

ABSTRACT. The Rh_2 (ap)$_4$ (2,2-*trans*) isomer (ap = 2-anilinopyridinate), which has two anilino nitrogens and two pyridyl nitrogens bound to each rhodium ion trans to their own kind, shows activation towards the one electron reduction of dioxygen at -0.40 V *vs* SCE. The ESR spectrum taken at 123 K proves the formation of a $[Rh_2(ap)_4(O_2)]$ ion with oxygen axially bound to one rhodium ion and the complex is at a Rh^{II}_2 oxidation state. The complex will form $[Rh_2(ap)_4(O_2)(CH_3CN)]^-$ in presence of CH_3CN/CH_2Cl_2 mixture without breaking the Rh-O^-_2 bond. When oxidized at -0.25 and 0.55 V, $[Rh_2(ap)_4(O_2)]$ will undergo two one electron oxidations to form $Rh_2(ap)_4(O_2)$ $[Rh_2(ap)_4(O_2)]^+$. Both species have an axially bound superoxide ion but the former is at $Rh^{II}Rh^{III}$ and the later at Rh^{III}_2 oxidation states. The ESR spectra and CH_3CN addition study, on the other hand, show that the later complex is better described as $[Rh_{II}Rh^{III}(ap)_4(O_2)]^+$ with the odd electron localized on rhodium ion and the complex has an axially

coordinated molecular oxygen. The electrochemical and ESR studies also show that the degree of dioxygen activation is a function of electrochemical redox potential.

INTRODUCTION

In recent years the electrochemical behavior of binuclear rhodium (II) complexes has received considerable attention in the literature.[1-12] The Rh-Rh bond distance,[13-16] the electronic spectra,[17-19] and the electrochemistry[20-22] of $Rh_2(O_2CR)_4$ and $Rh_2(O_2CR)_4$ $(L)_2$ have been investigated with respect to σ-donor and π-acceptor characteristics of the axial ligands, L, and the inductive effects of the substituents, R, on the carboxylato bridge. These studies have resulted in considerable disagreement concerning the nature of the metal-metal, and metal-ligand interactions.

The synthesis and spectroelectrochemical characterization of a dinuclear rhodium complex containing four 2-anilinopyridinate ligands (ap) was first reported by Tocher and Tocher[28]. The orientation of the bridging 2- anilino-pyridinate ions was not determined for the reported complex and it was not known which of the four possible geometric isomers was synthesized. Our laboratory was successful in obtaining two geometric forms of the tetrabridged complex.

Our recent study[29-31] shows that the complex $Rh^{II}Rh^{III}(ap)Cl$, where one rhodium ion is bound to four anilino nitrogens and a second rhodium ion is bound to four pyridyl nitrogens and one axial chloride (called the (4,0)isomer), can be reduced to generate $Rh^{II}_2(ap)_4$ with dissociation of chloride ion. The generated $Rh^{II}_2(ap)_4$ reacts rapidly with dioxygen to form $Rh^{II}Rh^{III}(ap)_4(O_2)$ where oxygen is bound to the rhodium ion with four pyridyl nitrogens. This species can be reduced at -0.48 V vs SCE to form $Rh^{II}_2(ap)_4(O_2)$. The presence of an oxygen scavenger will abstract the superoxide ion and regenerate $Rh^{II}(ap)_4$.

A more recent investigation shows that O_2 can undergo the oxidative coordination with $Rh^{II}Rh^{III}$ $(ap)_4(C\equiv CH)$ to form a formal Rh^{III}_2 (ap) $_4(C\equiv CH)$ (O_2) where dioxygen is bound to the rhodium ion with four anilino nitrogens. This is because the axial site of rhodium ion with four pyridyl nitrogens is occupied by the acetylenic group already. The oxidative coordination is caused by the axial ligand induced electron density on rhodium from the $C\equiv CH$ group. This dirhodium complex behaves much like an oxygen carrier and can undergo reversible O_2 binding. However, due to different binding site of O_2 on Rh^{II} $(ap)_4(O_2)$ and Rh^{II}_2 $(ap)_4$ $(C\equiv CH)$ (O_2) and the different oxidation states of the rhodium nuclei, no direct comparisons between the Rh-O_2 bond strength and the degree of O_2 activation can be made. Similar to the polarization of the odd electron dirhodium complexes, the degree of O_2 activation is obviously dependent not only on the oxidation states of the dirhodium units, but also on several other factors, such as the electron polarization caused by the kinds of bridging ligands, the different structural isomers, the steric hindrance created by four bridging ligands at the axial site, and the axial ligand induced electron density distribution. However, the detailed evaluation O_2 activation regarding to the dirhodium complexes is hampered by lack of literature data. This paper reports the formation of superoxide complexes of Rh^{II} $(ap)_4$, $Rh^{II}Rh^{III}$ $(ap)_4$ and Rh^{III} $(ap)_4$. The dirhodium complex, which has two pyridyl and two anilino nitrogens of the anilinopyridinate bridging ligands bound to each rhodium ion trans to their own kind, is one of four possible geometric isomers of $Rh_2(ap)_4$ compounds and is called the (2,2-$trans$) isomer. ESR characterization of (4,0) isomer form of $[Rh^{III}_2(ap)_4(O_2)]+$, which has not been previously reported, is also included. The com-

parison is made on the degree of O_2 activation vs the isomer effect, the Rh^{4+}_2/ Rh^{5+}_2 redox potential (electrochemical driving force) and the oxidation states of the rhodium ions.

EXPERIMENTAL SECTION

Chemicals. $RhCl_3 \cdot 3H_2O$ was obtained from Alfa Inorganics and used to prepare $Rh_2(OOCCH_3)_4$ by a literature method. The ligand 2-anilino-pyridine was purchased from Aldrich and recrystallized from hexane. Tetra-n-butylammonium perchlorate (TBAP, Fluka Chemicals) was recrystallized twice from ethanol and used as supporting electrolyte. All solvents were reagent grade and purified by standard procedure before used.

Preparation of Rh_2 (ap)$_4$ (A). It was prepared by the method described by Tocher and Tocher[28] which involves the the reaction of 0.5 g $RhCl_3 \cdot 3H_2O$ with an excess of the sodium salt of 2-anilinopyridine in refluxing ethanol. The yield is 22 % after recrystallization from CH_2Cl_2/hexane.

Preparation of Rh_2 (ap)$_4$Cl (B). It was synthesized by heating 100 mg of $Rh_2(O_2CCH_2)_4$ and 6 g of 2-anilinopyridine in a 50 ml round bottom flask at 130°C for 20 h under vacuum. At the end of the 20 h period, excess 2-anilinopyridine was removed by sublimation. The remaining mixture was dissolved in CH_2Cl_2 containing 50 % (v/v) CCl_4, placed on a silica gel column and eluted with a 5 % ethanol: 95 % methylene chloride solution. The red band was collected and solvent removed. The red solid was recrystallized from a mixture of CH_2Cl_2 and CH_3CN. A 40 % yield of B was obtained.

It should be pointed out that none of the reactants contain the chloride ion and yet the product contains an axial chloride. The chloride ion results from one or both of the following reactions: (1) Thermal or photochemical electron transfer from

$Rh_2(ap)_4Cl$ to CCl_4 which undergoes dissociative electron capture, or (2) the reaction of Rh_2 (ap)$_4$ Cl with dioxygen to form the superoxide complex $Rh_2(ap)_4O_2$, which reacts with CCl_4 or CH_2Cl_2 to abstract the chloride.

Instrumentation. ESR spectra were measured on a Brucker Model 100 E ESR spectrometer Cyclic voltammetric measurements were carried out on an IBM EC 225 voltammetric analyzer utilizing a three electrode configuration. The working electrode consisted of a platinum–buttom with surface area 0.19 mm. A saturated calomel electrode (SCE) was used as the reference electrode. For controlled potential coulometry, a BAS model SP-2 synthetic potentiostat was used. A Perkin-Elmer model 330 spectrometer was used to record electronic absorption spectra.

X-ray Data Collection and Processing. It was difficult to obtain a crystal of A which was stable in the X-ray beam long enough for X-ray analysis. A suitable crystal was finally obtained from a CH_2Cl_2 solution containing a small amount of benzonitrile. An extremely thin blackish–purple plate of A (A has one axially bound benzonitrile) having dimensions 0.50 × 0.50 × 0.04 mm was mounted

Table 1. X ray data collection and processing parameters

	Compound A	Compound B
space group	Pbca	I2/c
cell constantsa,A	21.002(7)	20.321(5)
b	17.317(6)	9.594(2)
c	26.028(8)	21.273(4)
		111.35)2)°
V, A^3	9466	3863
chemical formula	$Ph_2C_{51}H_{41}N_9$	$Rh_2C_{44}H_{36}N_8Cl$
formula weight	985.77	918.09
formula units per cell, Z	8	4
density (calc), g/cm^3	1.38	1.58
absorption coefficient, cm^{-1}	7.28	9.53
radiation (Mo K), A	0.71073	0.71073
$R(F_0)$	0.063	0.031
$R_w(F_0)$	0.074	0.028

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Table 2. Selected bond lengths (Å) and angles (°)

Length	A	B	Angle	A	B
Rh(1) Rh(2)	2.412(1)	2.406(1)	Rh Rh L(ax)	178.5(2)	180.00
Rh N(1)	2.042(9)	2.045(3)	Rh Rh N(1)	88.0(3)	86.7(1)
Rh N(2)	2.043(7)	2.009(4)	Rh Rh N(2)	87.2(2)	86.7(1)
Rh N(3)	2.051(8)	2.052(3)	Rh Rh N(3)	86.7(2)	86.4(2)
Rh N(4)	2.016(8)	2.008(3)	Rh Rh N(4)	88.0(3)	87.3(1)
RH N(5)	2.035(9)		Rh Rh N(5)	90.0(3)	
Rh N(6)	2.084(9)		Rh Rh N(6)	85.4(3)	
Rh N(7)	2.013(9)		Rh Rh N(7)	86.1(3)	
Rh N(8)	2.022(9)		Rh Rh N(8)	88.4(3)	
Rh L(ax)	2.189(10)	2.421(3)	Rh N(1)-C(5)	121.5(8)	118.3(3)
N(1) C(1)	1.36(1)	1.359(6)	Rh N(2) C(5)	123.9(7)	120.1(3)
N(1) C(5)	1.38(1)	1.362(6)	Rh N(2) C(6)	119.6(6)	120.0(3)
N(2) C(6)	1.46(1)	1.419(6)	Rh N(3) C(16)	119.8(7)	118.8(3)
N(3) C(12)	1.39(1)	1.367(6)	Rh N(4) C(16)	124.0(8)	119.3(3)
N(3) C(16)	1.41(1)	1.366(6)	Rh N(4) C(17)	116.4(7)	120.6(3)
N(4) C(16)	1.30(1)	1.355(6)	C(16) N(4) C(17)	117.0(10)	120.1(4)
N(4) C(17)	1.42(1)	1.406(5)	Rh N(5) C(27)	120.1(8)	
N(5) C(23)	1.31(1)		Rh N(6)-C(27)	123.0(8)	
N(5) C(27)	1.32(1)		Rh N(6)-C(28)	113.4(7)	
N(6) C(27)	1.35(1)		C(27) N(6) C(28)	122.4(9)	
N(6) C(28)	1.48(1)		Rh N(7) C(38)	122.6(8)	
N(7) C(34)	1.32(1)		Rh N(8) C(38)	120.9(8)	
N(7) C(38)	1.32(1)		Rh N(8) C(39)	118.9(8)	
N(8) C(38)	1.33(1)		C(38) N(8) C(39)	119.8(9)	
N(8) C(39)	1.45)1)		Rh N(9) C(45)	173.4(9)	
N(9) C(45)	1.13(1)		N(1)-C(5)-N(2)	115(1)	118.0(4)
			N(3) C(16) N(4)	116(1)	118.0(4)
			N(5) C(27) N(6)	118(1)	
			N(7) C(38) N(8)	118(1)	
			C(46) C(45) N(9)	178(1)	

on a glass fiber in a random orientation on an Enraf–Nonius CAD–4 automatic diffractometer. The radiation used was MoK α monochromatized by a dense graphite crystal assumed for all purposes to be 50 % imperfect. Crystallographic data are listed in *Table* 1. The Laue symmetry was determined to be mmm, and from the systematic absences noted the space group was shown unambiguously to be Pbca. Intensities were measured using the $\theta - 2\theta$ scan tecnique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability

and electronic reliability, and these did not very significantly. In reducing the data,Lorentz and polarization factors were applied, but no correction for absorption was made due to the small absorption coefficient. Unfortunately, the size of the crystal prevented more data from being collected.

A very small dark burgundy plate of **B** with approximate dimensions 0.25 × 0.25 × 0.10 mm was mounted on a glass fiber in a random orientation. Crystallographic data are also listed in *Table* 1. The Laue symmetry was determined to be 2/m, and from systematic absences noted the space group was shown to be either Ic or I2/c. The conventional setting C2/c (or Cc) was not used in this case since
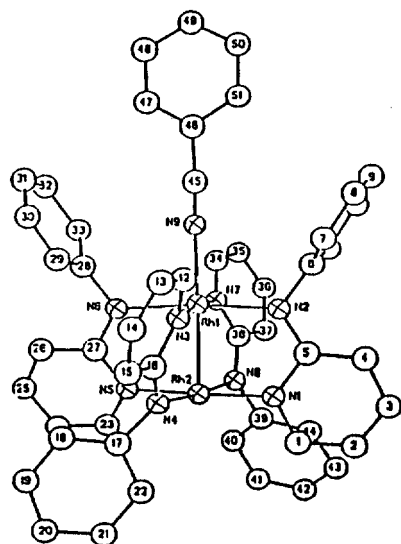
Fig. 1. ORTEP diagram of Rh₂(ap)₄(C₆H₅CN) (2,2 *trans*) isomer.

Fig. 2. ORTEP diagram of Rh₂(ap)₄Cl (4.0) isomer.

this would have a β angle much further from 90° (the C centered cell has a = 23.47, b = 9.59, c = 21.27 Å, and β = 126.2°). All other procedures and methods used for structure determination were the same as described for **A**.

The selected bond distances and angles for **A** are listed in *Table* 2. A labelled ORTEP diagram of the molecule is presented in *Fig.* 1. The Rh–Rh bond distance of 2.412 Å falls within the expected range for dirhodium (II,II) complexes. The average Rh–N_p and Rh–N_a bond distances are 2.035 and 2.041 Å, A 14.3 degree average torsional twist of the equatorial planes of the two rhodium ions was observed for the complex. The selected bond distances and angles for **B** are listed in *Table* 2. A labelled ORTEP diagram of the molecule is shown in *Fig.* 2. The prominent feature of the structure is the arrangement of the bridging ions such that all four pyridyl nitrogens are bound to one rhodium, Rh(1), with an average Rh–N_p distance of 2.048 Å. The second rhodium, Rh(2), is bound equatorially to four anilino nitrogens with an average Rh–N_a bond distance of 2.008 Å. The Rh–Rh and Rh–Cl bond distance are 2.046 and 2.421 Å. A large average torsional angle of 23.4 degrees was found.

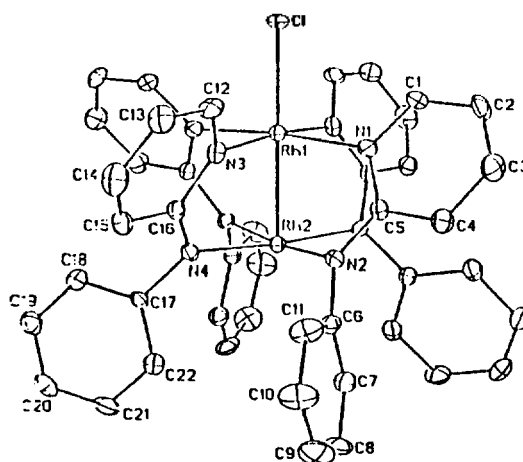## RESULTS AND DISCUSSION

O_2 Reduction by the (2,2-*trans*) isomer of Rh_2 (ap)₄. The molecular structure of (2,2-*trans*) isomer of Rh_2(ap)₄ is illustrate in *Fig.* 1 which shows that each rhodium ion is surrounded by two anilino and two pyridyl nitrogens trans to their own kind and there is an axially coordinated benzonitrile, which is used to grow the crystal. Since the bridging ligand creates an identical environment on both rhodium ions, the complex does not show any polarization effect caused by the bridging ligands. This is shown by the ESR spectrum of [Rh_2 (ap)₄]⁺ (the singly oxidized Rh_2 (ap)₄), which shows a g_3 singnal split into a 1:2:1 triplet.[33] A labelled ORTEP diagram of the Rh₂(ap)₄Cl is shown in *Fig.* 2. The prominent is arrangement of the bridging ions such that all four pyridyl nitrogens are bound to one rhodium, Rh(1), with an average Rh–N_p distance of 2.048 Å. The Rh–Rh and Rh–Cl bond distances are 2.406 and 2.421 Å. A large average torsional angle of 23.4 degree was found. Cyclic voltammograms of **A** and **B** in methylene chloride under Ar and O_2 are shown in *Fig.* 3.

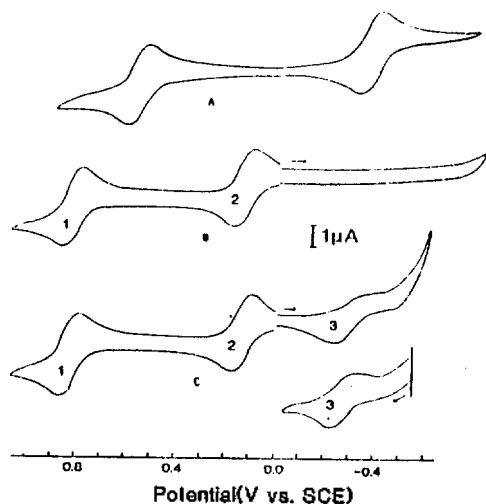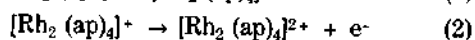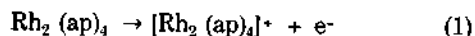The two oxidation of **A** correspond to reactions 1 and 2 under Ar in a non–bonding solvent such

Fig. 3. Cyclic voltammograms of (a) (4.0) isomer in CH$_2$Cl$_2$, 0.1M TBAP, and (2,2 *trans*) isomer (b) under Ar, (c) under O$_2$ and (d) under O$_2$ and the initial scan started at -0.70 V. The scant rate is 0.1 V/s.

as CH$_2$Cl$_2$.

$$Rh_2 (ap)_4 \rightarrow [Rh_2 (ap)_4]^+ + e^- \qquad (1)$$

$$[Rh_2 (ap)_4]^+ \rightarrow [Rh_2 (ap)_4]^{2+} + e^- \qquad (2)$$
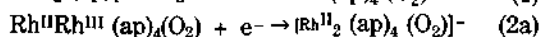
The half wave potentials for reactions 1 and 2 are located at $E_{1/2} = 0.08$ and 0.82 V in Ch$_2$Cl$_2$, 0.1 M TBAP, respectively. Values of $|E_{pa}-E_{pc}|$ vary between 60 and 70 mV at a scan rate of 0.2 V/s, while $i_{pa}/i_{pc} = 1$ and $i_p/V^{1/2}$ are invariant with increasing sweep rate, indicating that these are diffusion-controlled on electron transfer processes.

The electrochemistry of **B** under Ar is characterized by a reversible on electron reduction at $E_{1/2} = -0.38$ V and reversible on electron oxidation at $E_{1/2} = 0.52$ V in CH$_2$Cl$_2$, 0.1 M TBAP. These values for **B** are shifted cathodically by 300 to 460 mV compared to E values for **A** under the same experimental conditions. The more negative potentials of **B** result from the different bonding arrangement of the bridging ligands (isomer effect) and the presence of the axially bound chloride (**A** contains no axial Rh-Cl bond).
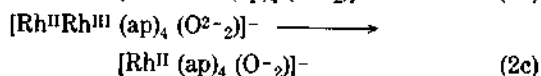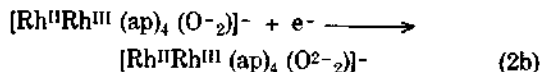
Fig. 3b illustrates the cyclic voltammogram of Rh$_2$ (ap)$_4$ in CH$_2$Cl$_2$, 0.1 M TBAP, which shows

that the complex has two oxidation waves at $E_{1/2} = 0.07$ and 0.82 V, corresponding to the formation of Rh^{II}Rh^{III} and Rh$_2^{III}$ oxidation states. Both oxidations are significantly shifted cathodically from the same oxidation waves of Rh$_2$ (ap)$_4$ (4,0) isomer[33] which occur at -0.38 and 0.52 V, respectively. When O$_2$ is bubbled through the solution, both two oxidations showed little change and, at the same time, there is a new reduction wave ($E_{1/2} = -0.48$ V) observed at $E_{1/2} - 0.40$ V (wave 3, *Fig.* 3c). This wave is not totally reversible in a sence that the cathodic wave is smaller than the andic wave. However, when the initial potential scan starts at -0.65 V and the scan potential is switched at -0.2 V, wave 3 becomes a reversible electron transfer process (*Fig.* 3d). Similar reduction wave ($E_{1/2} = -0.48$ V) has been observed for the catalytic reduction of O$_2$ in CH$_2$Cl$_2$ in presence of the (4,0) isomer.[29] This wave corresponds to the reduction of the oxygen adduct Rh^{II} Rh^{III} (ap)$_4$ (O$_2$):

$$Rh^{II}_2 (ap)_4 + O_2 \rightarrow Rh^{II}Rh^{III} (ap)_4 (O_2) \qquad (1)$$
$$Rh^{II}Rh^{III} (ap)_4(O_2) + e^- \rightarrow [Rh^{II}_2 (ap)_4 (O_2)]^- \qquad (2a)$$

when the redox potential of both (2,2-trans) and (4,0) isomers are compared, the $E_{1/2}$ values of process 3 are very similar for both complexes even though the redox potentials for Rh$^{4+}_2$/Rh$^{5+}_2$ and Rh$^{5+}_2$/Rh$^{6+}_2$redox couples differ quite significantly. The similar potential values for wave 3 of both compounds indicates that, insted of having the electron transferred from the electrode directly to the rhodium ion, i.e. a metal centered reduction, the electron transfer may be an route through the bound dioxygen followed by an intramolecular electron transfer to form [Rh$^{II}_2$ (ap)$_4$ (O$_2$)]$^-$:

$$[Rh^{II}Rh^{III} (ap)_4 (O^-{}_2)]^- + e^- \longrightarrow$$
$$[Rh^{II}Rh^{III} (ap)_4 (O^{2-}{}_2)]^- \qquad (2b)$$
$$[Rh^{II}Rh^{III} (ap)_4 (O^{2-}{}_2)]^- \longrightarrow$$
$$[Rh^{II} (ap)_4 (O^-{}_2)]^- \qquad (2c)$$

The charges on oxygen in these reactions are

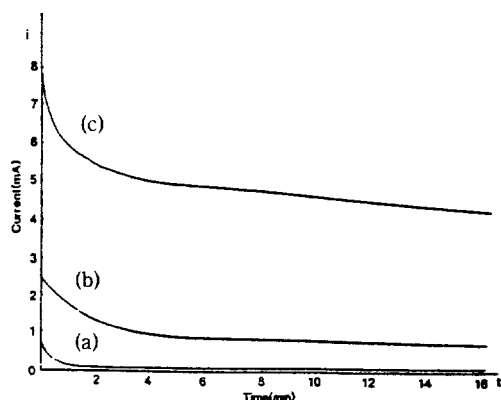*Fig.* 4. Current time curves of the controlled potential reduction of the CH_2Cl_2 solution at -0.65V *vs* SCE. (a) in blank solution under O_2, (b) solution containing (2,2 *trans*) isomer under O_2 and (c) solution b with 0.1 *M* benzoic anhydride.

assigned to indicate the formation of peroxide and superoxide ions. However, the definite assignment of the electron transfer mechanism is still pending on the further study. The lack of potential shifts in the first and second oxidation of Rh_2 (ap)$_4$ under O_2 and Ar probably indicates a week interaction mechanism between Rh_2 (ap)$_4$ and O_2.

The neutral Rh_2 (ap)$_4$ species is unambiguously assigned as Rh(II)-Rh(II). The oxidation state assignment after bound with dioxygen is not so clear. The assignment depends on whether the bound dioxygen is a neutral O_2 molecule or a superoxide ion. The (4,0) compound, which has been studied before,[29] shows the strong polarization of the electron density in the dirhodium unit. A Rh(II)-Rh(II) oxidation state in this compound actually behaves like a Rh(I)-Rh(II) complex. The difference in the electron polarization between these two complexes is demonstrated by the big difference in their redox potentials and in degree of the O_2 activation. For example, (4,0) isomer at Rh(II)-Rh(II) oxidation state will react with O_2 very rapidly to form Rh_2 (ap)$_4$ (O_2) upon exposure to the air as proven by a rapid color change from green to brown of the solution. The (2,2-*trans*) isomer is relatively stable and the neutral com-

pound with and Rh(II)-Rh(II) oxidation state and no axially bound O_2 is easy to obtain. However, when the CH_2Cl_2 solution containing (2,2-trans) isomer is bubbled with pure O_2 the color of the solution will slowly change from green to brownish, indicating the partial formation of the dioxygen adduct.

The (4,0) isomer has been shown to catalytically reduced O_2 in presence of a superoxide scavenger as thermodynamic driving force. The (2,2-*trans*) isomer also displays similar properties as shown in *Fig.* 4, which illustrates current-time curves of the complex in CH_2Cl_2, 0.1 *M* TBAP, under controlled potential electrolysis condition As shown in *Fig.* 4 (curve a) O_2 does not reduce at a controlled reduction potential of -0.65 V. When the (2,2-trans) isomer is added into the solution the current is much higher and the residual current is also very persistent (a reduction of the complex under Ar will result in a decreased residual current which rapidly approaches zero). This residual current is due to the catalytic reduction of the O_2 by one electron to form the superoxide. The thermodynamic driving force is again provided by the reaction of the superoxide ion with the CH_2Cl_2 solvent molecules.[29] When 0.1 *M* benzoic anhydride is added to the solution, the residual current is increased by a factor of five. It is already known that benzoic anhydride reacts with superoxide ion to form the benzoic acetate ion[35.35] and so causes an increase of electrolysis current.

ESR Studies of Dioxygen Binding. The ESR spectra of both (4,0) and (2,2-*trans*) isomers have been reported in previous studies. The (4,0) isomer shows an axial signal with g_I = 2.08 and g_{II} = 1.95 which is a doublet due to the polarization of the odd electron on one rhodium ion. The singly oxidized (2,2-*trans*) isomer gives a rhombic signal with g_3 = 1.94 which is a 1:2:1 triplet due to delocalization of the odd electron on both rhodium ions. The reported (4,0) isomer dioxygen adduct, [Rh_2 (ap)$_4$ (O_2)]$^-$, also shows a rhombic signal with
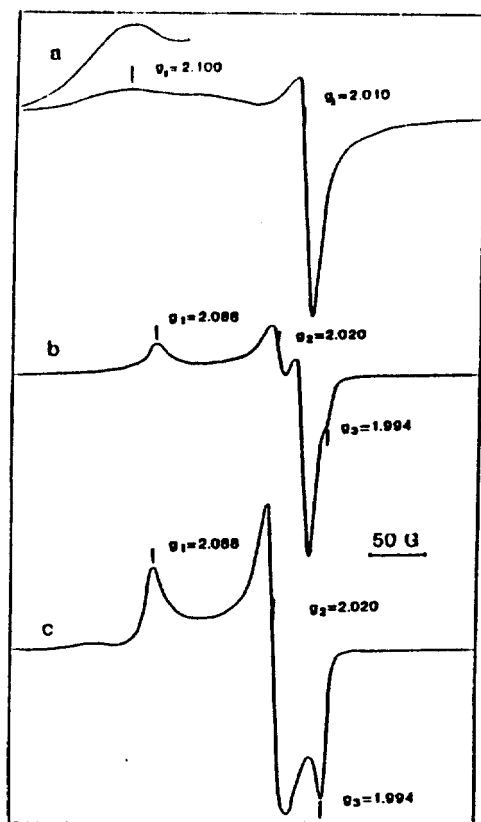
Fig. 5. ESR spectra of (a) O_2 reduced at -0.65 V, (b) $Rh_2(ap)_4(2,2\text{-}trans)$ isomer reduced at -0.65V under O_2 and (c) solution b oxidized at -0.25 V in THF, $0.1M$ TBAP. All spectra were taken at 123 K.

g_1 = 2.10, g_2 = 2.01 and g_3 = 1.99 in CH_2Cl_2 and indicates the formation of superoxide complex.[29] The neutral (2,2-*trans*) complex does not have ESR spectrum neither does its dioxygen adduct. The signal due to the free O_2^- ion is not observed because it is well known that this ion will react with CH_2Cl_2.[36]

The controlled potential electrolysis of a blank THF solution, $0.1 M$ TBAP, at -0.65 V under O_2 without dirhodium complex will generated an axial signal with $g_{||}$ =2.100 and $g_\perp$ = 2.010, corresponding to free O_2^- (*Fig.* 5a). Even though the cyclic voltammogram of O_2 in THF shows that dioxygen will not be reduce until - 0.8 V, a small amount of O_2^- is still generated under the condi-

tion of the bulk electrolysis. This is either due to that the potential setting is close to the foot of the reduction wave, or the cyclic voltammetric wave of O_2 in THF is a broad, irreversible peak, and probably extends into the potential setting range. Similar O_2-spectrum has been reported in DMSO with $g_{||}$ = 2.104 and $g_\perp$ = 2.007.[37] The ESR spectrum of the product generated from the reduction the (2,2-trans) isomer in THF under O_2 at -0.65 V is shown in *Fig.* 5b. We notice that this spectrum is a combination of free O_2^- signal and $[Rh_2(ap)_4(O_2)]^-$ signal when *Fig.* 5a and 5b are compared. When the electrolysis potential is stepped to -0.25 V and the ESR is taken again at 123 K, the spectrum shown in *Fig.* 5c is obtained and gives g_1 = 2.088, g_2 = 2.020 and g_3 = 1.994. This signal is due to the residual $[Rh_2 (ap)_4 (O_2)]^-$ which is not completely oxidized at this potential setting, while free O_2^- is reoxidized. The observed signal in *Fig.* 5c is very similar to the one obtained for the (4,0) isomer superoxide adduct.[29] However, due to the trace O_2^- that can be generated at -0.65 V in THF solution, we are not able to tell wether the (2,2-*trans*) isomer superoxide adduct is generated by reaction of Rh (ap)$_4$ with free O_2^- ion or by direct electroreduction of Rh_2 (ap)$_4$ (O_2) under O_2, this is probably the species that is directly reduced at the electrode to form $[Rh_2 (ap)_4 (O_2)]^-$.

The product generated from the controlled potential reduction of the (2,2-*trans*) isomer at -0.65 V in CH_2Cl_2 under O_2 clearly shows a rhombic signal with g_1 = 2.062, g_2 = 2.016 and g_3 = 1.971, and no splitting due to Rh (I = 1/2) is observed (solid line, *Fig.* 5a). This spectrum again indicates the formation of the (2,2-*trans*) isomer superoxide adduct, $[Rh_2 (ap)_4 (O_2)]^-$. The odd electron is primary located on the axial coordinated O_2, implying the formation of the superoxide adduct. Due to the different geometric arrangements of the bridging ligands, superoxide adducts of the
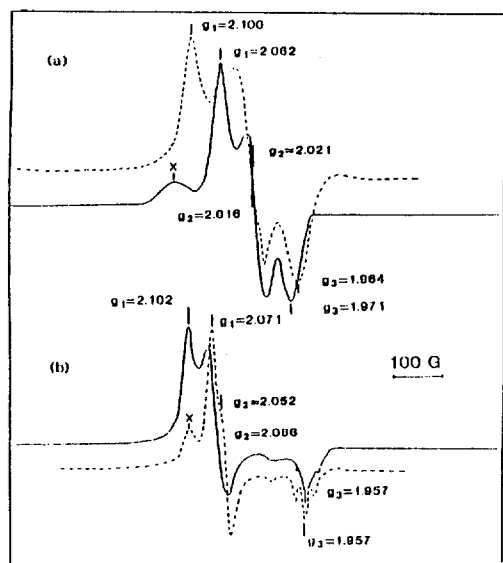
Fig. 6. ESR spectra of (a) the $Rh_2(ap)_4(2,2$ *trans*) isomer reduced at -0.65 V under O_2 in CH_2Cl_2 at -0.65 V (solid line), with added $1M$ CH_3CN (dashed line), and (b) the $Rh_2(ap)_4(2,2$ *trans*) isomer oxidized in CH_2Cl_2 at 0.55 V (solid line), with added $1M$ CH_3CN (dashed line). All spectra were taken at 123K.

(4,0) and (2,2-*trans*) isomers have similar ESR spectra but different g values. A small signal is observed at g = 2.12 (marked x) and is probably cause by the side products form the reaction of O_2^- with solvent molecules. It is interesting to see that, similar to the result obtained in the case of (4,0) isomer, the free O_2^- signal is not observed in this solvent, even though the ESR spectrum of the free superoxide ion has been reported in CH_2Cl_2-acetone-methanol mixture system.[38,39] When CH_3CN is added to the [Rh_2 (ap)$_4$ (O_2)]-CH_2Cl_2 solution, a new signal is observed at $g_1 = 2.100$, $g_2 = 2.021$ and $g_3 = 1.964$ (dashed line, *Fig.* 6a). The singal is very similar to that obtained in pure CH_2Cl_2 and indicates that O_2^- is stil bound to the dirhodium unit. This signal should be the spectrum of [Rh_2 (ap)$_4$ (O_2) (CH_3CN)]- with CH_3CN coordinated to the dirhodium unit trans to the bound dioxygen. However, the cyclic voltammogram of the (2,2-*trans*) isomer in pure CH_3CN does not show the reduction process 3 illustrated

in *Fig.* 3 neither does the superoxide adduct signal shown on the ESR spectrum taken after electroreduction at -0.65 V. This is probably due to formaiton of a bis CH_3CN adduct of the (2,2-*trans*) isomer and the O_2 activation and superoxide binding are completely depressed in this solvent.

When the reduction potential is stepped back to -0.20 V a similar ESR spectrum as that shown in *Fig.* 6 (dashed line), with decreased intensity is obtained, probably due to the residual reduced form of [Rh_2 (ap)$_4$ (O_2)]-, since Rh_2 (ap)$_4$ (O_2) does not show any ESR signal. This is proved by the lack of ESR signal of the neutral (2,2-*trans*) Rh_2 (ap)$_4$ compound taken in CH_2Cl_2 under O_2. When the electrolysis patential of $Rh_2(ap)_4$ in CH_2Cl_2 under O_2 is stepped further to +0.55 V, an ESR spectrum is again recorded as shown in *Fig.* 6b (solid line). The asymetric signal with $g_1 = 2.102$, $g_2 = 2.071$ and $g_3 = 1.957$ clearly indicates that dioxygen is still bound to the rhodium unit with formation of [Rh_2 (ap)$_4$]$^+$. The g_3 value is very close to the value observed for [Rh_2 (ap)$_4$]$^+$ in the same solvent but there is not splitting due to Rh nuclei. Even though this species can be formally written as the superoxide addcut of the Rh_2^{III} unit, the observed g_3 signal and its a value suggests that the complex probly has a $Rh^{III}Rh^{II}$ center with an axially coordinated dioxygen rather than a superoxide ion. This assignment is further proven by the ESR spectrum of the solution after adding CH_3CN as shown in *Fig.* 6b (dashed line). Even though some [Rh_2 (ap)$_4$ (O_2)]$^+$ is still left over (marked x in Fig. 6b) due to incomplete reaction, the ESR spectrum clearly indicates the formation [$Rh_2(ap)_4$]$^+$ or, more accurately, [$Rh_2(ap)_4$ (CH_3CN)$_2$]$^+$ with loss of molecular oxygen, not superoxide ion. These spectra suggest the following reactions.

$$Rh_2\ (ap)_4\ (O_2) \longrightarrow$$

$$[Rh_2\ (ap)_4\ (O_2)]^+ + e^- \qquad (3)$$

$$[Rh_2\ (ap)_4\ (O_2)]^+ + 2CH_3CN \longrightarrow$$

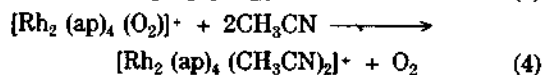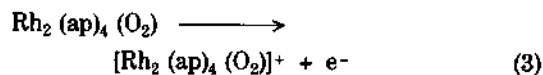$$[Rh_2\ (ap)_4\ (CH_3CN)_2]^+ + O_2 \qquad (4)$$

Table 3. ESR data of two dirhodium complexes and their dioxygen adducts

Compound	Solvent		electro E	g_1	g_2	$g_3(A_3 \times 10^4 cm^{-1})$
(2,2 *trans*) isomer						
[Rh$_2$(ap)$_4$]$^+$,[a]	CH$_2$Cl$_2$	Ar	0.55	2.08	2.06	1.96 (15.6)
[Rh$_2$(ap)$_4$(CH$_3$CN)$_2$]$^+$	CH$_3$CN	O$_2$	0.55	2.062	2.016	1.971 (···)
[Rh$_2$(ap)$_4$(O$_2$)]$^+$	CH$_2$Cl$_2$	O$_2$	0.55	2.100	2.021	1.964
Rh$_2$(ap)$_4$(O$_2$)	CH$_2$Cl$_2$	O$_2$	—	—	—	—
[Rh$_2$(ap)$_4$(O$_2$)]$^-$	THF	O$_2$	-0.65	2.088	2.020	1.994
[Rh$_2$(ap)$_4$(O$_2$)]$^-$,[b]	CH$_2$Cl$_2$	O$_2$	-0.65	2.071	2.052	1.957
[Rh$_2$(ap)$_4$(CH$_3$CN)(O$_2$)]$^-$	CH$_3$CN	O$_2$	-0.65	2.102	2.066	1.957
(4,0) isomer						
[Rh$_2$(ap)$_4$(O$_2$)]$^+$	THF	O$_2$	0.70	?	?	?
Rh$_2$(ap)$_4$(O$_2$)	CH$_2$Cl$_2$	O$_2$	—	—	—	—
[Rh$_2$(ap)$_4$(O$_2$)]$^-$	CH$_2$Cl$_2$	O$_2$	-0.65	2.094	2.026	1.998
[Rh$_2$(ap)$_4$(O$_2$)]$^-$	THF	O$_2$	-0.65	2.096	2.027	2.000
				$g_\perp$	$g\|(A\| \times 10^4 cm^{-1})$	
Rh$_2$(ap)$_4$Cl,[a]	CH$_2$Cl	Ar	—	2.09	1.95 (26.4)	
O$_2^-$	THF	O$_2$	-0.65	2.100	2.010	

[a]Data taken from ref. 33. [b]Data taken from ref. 29.

Reaction 4 indicates that the singly oxidized (2,2-*trans*) isomer behaves much like an oxygen carrier. The lack of O$_2$ activation from the dirhodium complex with higher oxidation state is then associated with the electron donor ability of the rhodium ion, which in turn is controlled by its oxidation state and the equatorially coordinated ligands.

The formation of (4,0) isomer superoxide adduct has also been studied and the complex shows a similar spectrum as the one of the (2,2-*trans*) isomer. The g values of [Rh$_2$ (ap)$_4$ (O$_2$)]$^-$ and [Rh$_2$ (ap)$_4$ (O$_2$)]$^+$ are listed on *Table* 3. for comparison.

In summary, the dirhodium complex are clearly active toward the dioxygen activation through one electron transfer process. The degree of O$_2$ activation is controlled by the electron donor ability of the rhodium ion. The rhodium ions with lower oxidation states are better O$_2$ activation agents than the one with higher oxidation state, while the later is best described as an oxygen carrier. This study reported the formation of the dirhodium oxygen adduct with formal Rh^{II}$_2$, Rh^{II} Rh^{III} and Rh^{II}$_2$ oxidation states. When both (2,2-*trans*) and (4,0) isomers with Rh^{II}$_2$ oxidation states are compound, the one with more negative Rh^{4+}$_2$/Rh^{5+}$_2$ redox couple has higher activity towards the O$_2$ reduction, due to the larger thermodynamic driving force. In this case, both the less steric hindrance and the larger electron polarization on the (4,0) isomer made the complex more active toward the O$_2$ activation than (2,2-*trans*) isomer.

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