To the Graduate Council:

I am submitting herewith a thesis written by Peter Wilburn Tinsley entitled "Electrochemical Investigation and Synthesis of Some Rhodium Dimers." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Clifton Woods

Clifton Woods, Major Professor

We have read this thesis
and recommend its acceptance:

William T Bell

James Q. Chambers

Accepted for the Council:

L Evans Haith

Vice Chancellor
Graduate Studies and Research

ELECTROCHEMICAL INVESTIGATION AND SYNTHESIS OF SOME RHODIUM DIMERS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Peter Wilburn Tinsley

August 1981

DEDICATION

As is my life, this work is dedicated to Wendy Warner Tinsley.

ACKNOWLEDGEMENTS

The author would not have this opportunity if it were not for the excellent guidance and support of Dr. Clifton Woods, III. His advice was priceless if not always followed.

The following folks have made my research much simpler: Don Womack, Paul Enlow, Richard Crocombe, Arlene Garrison, Rob Peterson, Dr. J. Q. Chambers and Billy Anderson.

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ABSTRACT

The electrochemical behavior of several rhodium(I) dimers containing two bridging bis(diphenylphosphino)methane or bis(diphenylarsino)methane ligands have been examined using voltammetry and bulk electrolysis in the nonaqueous solvent methylene chloride. The effect of adding coordinating ligands such as halide ions and carbon monoxide to the electrochemical system has been observed.

Several new rhodium(II) dimers have been prepared by the oxidation of the rhodium(I) dimers in the presence of excess chloride or bromide ions. The reduction of a rhodium(I) dimer in the presence of excess carbon monoxide has also been examined. An isolable reduction product has been prepared. The oxidation and reduction products have been characterized using infrared spectroscopy, UV-Visible spectroscopy and elemental analysis.

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CHAPTER I

INTRODUCTION

It has been known since the discovery of transition metal complexes that the behavior of the metal atom or ion is dependent on the nature of the coordinated ligands. This dependence is even seen in complexes of a given metal in which the structural arrangement of the ligands and the electronic configuration of the metal are the same. Since transition metals can exist in several oxidation states, the stability of a given oxidation state and thus the ability of the metal complex to undergo oxidation-reduction reactions are also dependent on the nature of the coordinated ligands. For this reason coordination complexes are amenable to investigation by electrochemical methods.

Electrochemical oxidation or reduction can be more specific than chemical procedures since one can set the desired potential and oftentimes obtain unusual oxidation states which might be difficult or impossible to obtain by chemical means. This control of potential also provides, through coulometry, the ability to not only ascertain the number of electrons being transferred in the process but also makes it possible to synthesize in bulk and isolate some of these more unusual complexes.

Cyclic voltammetry can be a powerful tool for the chemist concerned with redox reactions of metal complexes. The ability to sweep the potential in both the positive and negative directions in a cyclic voltammetric experiment allows one to obtain a quick overview of the redox reactions which occur within the electrochemical limits of the solvent

medium. It is oftentimes possible to observe intermediates which are only stable on the cyclic voltammetry time scale.

Even with the tremendous potential of electrochemical methods in generating new metal complexes and in conducting studies of the mechanistic aspects of redox reactions of metal complexes, there are still many metal complexes whose electrochemical behaviors have not been heavily investigated. Rhodium complexes fall into this category.

The few electrochemical studies which have been conducted on rhodium complexes have focussed mainly on monomers; however, several dimers have reportedly been formed during the early polarographic studies of these monomers. Pilloni and coworkers for example reported observing the formation of $[Rh(CO)(PPh_3)_3]_2$ as one of the reduction products of $RhCl(CO)(PPh_3)_2$ in the presence of excess PPh_3.[1] Likewise, through exhaustive controlled-potential electrolysis, de Montauzon and Poilblanc were able to isolate products of the type $[Rh(solvent)(CO)(PMe_2Ph)_2]_2$.[2] In one of the few reported studies involving the cyclic voltammetry of rhodium monomers, Olson and Keim suggest the formation of a rhodium dimer.[3] This dimer resulted from the initial generation of the paramagnetic rhodium monomer $Rh(PPh_3)_4$ which subsequently dimerized to give the diamagnetic Rh(0) species $[Rh(PPh_3)_4]_2$.

Even though the ability of a metal to attain various oxidation states is usually regulated by the ligands in the inner coordination sphere, potential ligands in the solvent medium can drastically affect the redox properties of a complex either by ligand addition or substitution. The effect of these ligands on the redox properties of the metal complex can usually be attributed to either the efficiency of the ligand in donating or accepting electrons or to the ligand's steric requirements.

Many ligands which are known as π-acid ligands can not only donate electrons but can also accept electrons from the central metal. A ligand normally donates a σ electron pair to an empty orbital on the metal. Simultaneously, an empty π orbital on the ligand might be oriented such that there is overlap with an occupied metal π orbital. This σ donor-π acceptor mechanism is known as backbonding. The strengths of the σ and π bonds are functions of the ligand for a given metal ion. A complex which contains such ligands can often accommodate different oxidation states simply by shifting the electron density to or from the ligands involved. One such π-acid ligand which has received considerable attention and which will be of interest in the work described in this thesis is carbon monoxide (CO). Carbon monoxide is generally accepted to be a weak σ donor and a strong π acceptor. Due to the ability of CO to accept d_π electrons into its π^* orbitals (Figure 1), it is able to stabilize metals in low oxidation states.

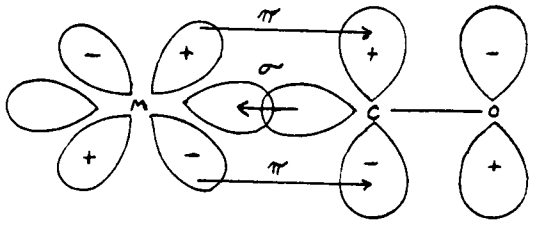


Figure 1. The σ donor-π acceptor mechanism of CO bonding with transition metals.

If the metal is in a low oxidation state it can donate electrons to the CO through the strong π bond, but because of the weak σ donor nature of the CO, the metal is not forced to accept much electron density from the CO.

The degree of backbonding and mode of bonding in carbonyl complexes can be monitored using infrared spectroscopy. If the π electron density donated by the metal to the CO is reduced, the C-O bond order and vibrational force constant are raised, thus an increase in the carbonyl stretching frequency will be observed. The difference between terminal and bridging carbonyls is illustrated by the fact that terminal carbonyls in rhodium complexes exhibit an infrared band in the region of 2050-1950 cm^{-1} while bridging carbonyls are usually observed in the 1860-1750 cm^{-1} region.

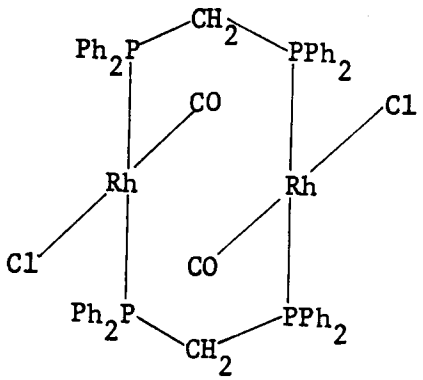
The research described in this thesis will also involve the use of isocyanides (RNC) as ligands. The bonding of RNC ligands is similar to that of CO but they are better σ donors and poorer π acceptors than CO. Metals in high oxidation states will therefore favor RNC over CO as ligands. The N-C stretching frequencies in rhodium isocyanide complexes are usually found around 2200-2100 cm^{-1} and are affected in a manner similar to the carbonyls when the degree of backbonding is altered.

As noted earlier, coordinated ligands can inhibit a metal from undergoing a change in oxidation state. This can occur if the coordinated ligands sterically block the adoption of a configuration which is more stable for the new oxidation state. The coordinated ligands can also interfere with attempts of a free ligand, such as CO, to bond with the metal and thereby stabilize the new oxidation state. This would imply that potential ligands which are present in the medium during cyclic voltammetry might coordinate with the metal complex when a different oxidation state is adopted by the metal. These potential ligands can either be solvent molecules, the supporting electrolyte ions or a species

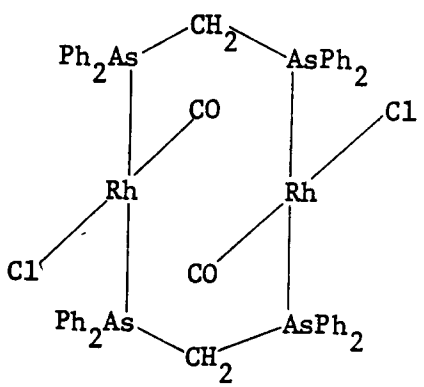
which has been added to the solution for the specific purpose of coorinating to the metal.

In order to study the role which ligands play in determining the electrochemical properties of rhodium dimers it is necessary to study similar complexes and to have some understanding of how slight changes in ligand properties alter the structural and chemical behaviors of these complexes. Two ligands of interest in this study are bis(diphenylphosphino)methane (dpm) and bis(diphenylarsino)methane (dam).

When dpm or dam are added to $Rh_2(CO)_4Cl_2$ in a 4:1 ratio, complexes 1 or 2 are formed, respectively. These two complexes are known from X-ray crystallography to be isostructural.[4,5]



1



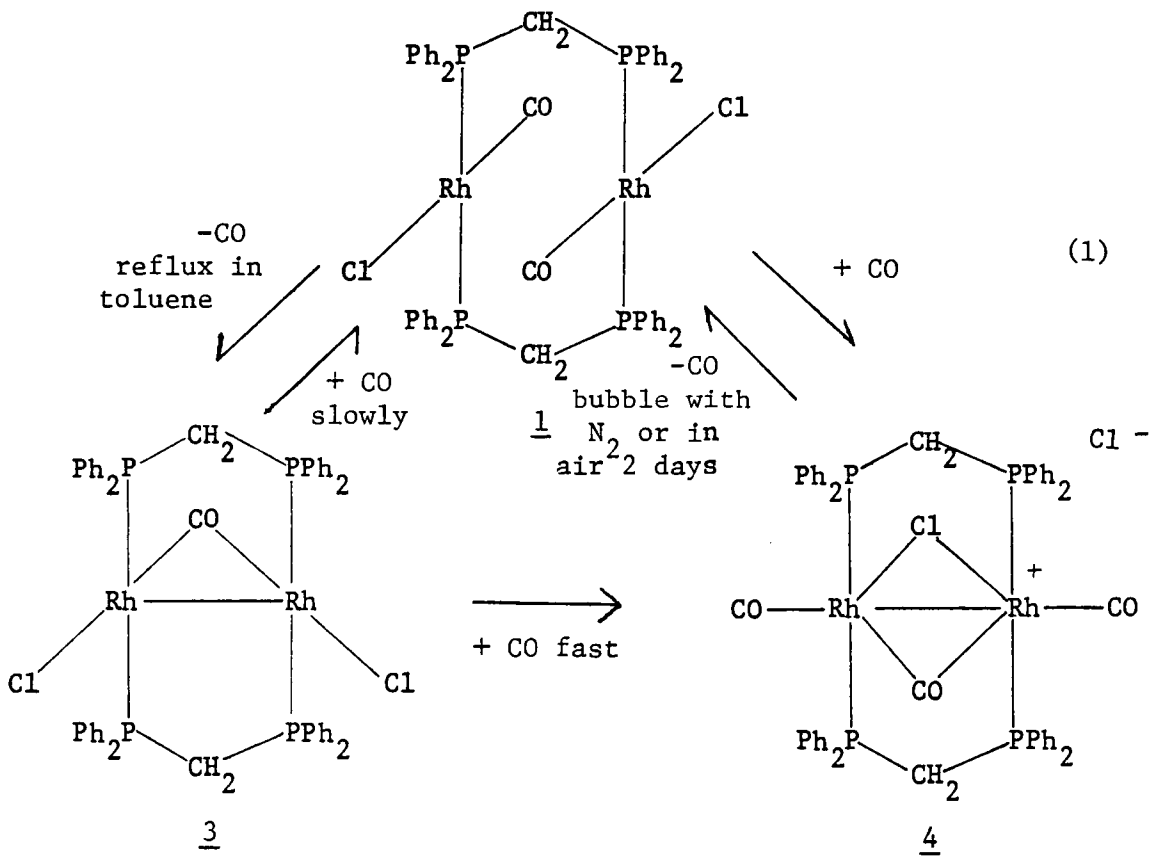
2

Complex 1 is insoluble in most solvents whereas complex 2 is more soluble in the same solvents.[5,6] It was for this reason that the isostructural nature of 1 and 2 was originally questioned. Even though X-ray crystallography resolved the question of structural similarities, it was inconclusive in providing explanations for the solubility differences. It was shown that 1 has a high efficiency for packing, thus causing lower solubility, yet the same is true for 2. The bite size (distance between two rhodiums) was found to be considerably larger for 2 (3.391(1) A) than for 1 (3.2386(5) A). The repulsive effect between the two rhodium centers

was also illustrated in that the P-C-P angle was greater than the As-C-As angle, thus causing the dpm to be strained. These differences can be considered to be primarily due to the larger radius of arsenic compared to phosphorus. The smaller bite size of 1 (p 5) and its strained P-C-P angle may contribute to the ability of small bridging ligands to form stable complexes with 1 (p 5) and not with 2 (p 5).[5]

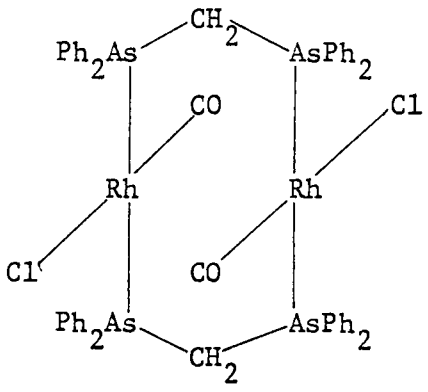
As with solubility, it was later found that there are extreme differences in the chemical properties of 1 (p 5) and 2 (p 5). Both 1 (p 5) and 2 (p 5) exhibit, to some extent, an ability to coordinate RNC[7] and additional CO[8] as well as undergo halide exchanges[5]; however, there are very few cases where both 1 (p 5) and 2 (p 5) give analogous products.

One important example of this dissimilar nature is the ability of 1 (p 5) to form the stable complexes 3 and 4 by losing or accepting CO, respectively (Equation 1).



(1)

Under similar conditions complex 2 (p 5) does not form stable products. It has been suggested, however, that in the presence of excess CO, 2 (p 5) is in equilibrium with a complex analogous to 4 (p 6) but attempts to precipitate this complex led to the recovery of 2 (p 5) (Equation 2).[8]



2

$$\xrightarrow{+\ CO} \text{Starting Material Isolated} \qquad (2)$$

The conversion of 1 (p 5) to 4 (p 6) and 4 (p 6) back to 1 (p 5) by simply bubbling with CO and N_2 respectively, makes these systems convenient for electrochemical studies. It was experimentally observed during the conversion of either 3 (p 6) or 4 (p 6) back to 1 (p 5), that loss of the CO also occasions the loss of the rhodium-rhodium bond.[5,8]

Complexes 3 (p 6) and 4 (p 6) represent a new class of metal dimers which are presently the subject of considerable investigation.[9] Complexes with structures illustrated by 3 (p 6) have come to be known as A-Frame complexes. These A-Frame complexes are composed of two dpm ligands which form the binuclear complex. The small molecule (B) causes the approximate square planar metals (M) to be oriented such that the out-of-plane metal d and p orbitals form a "pocket" or "active site" into which another small molecule can bind (Figure 2, p 8).[10]

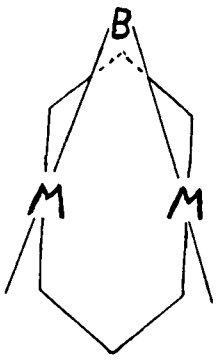
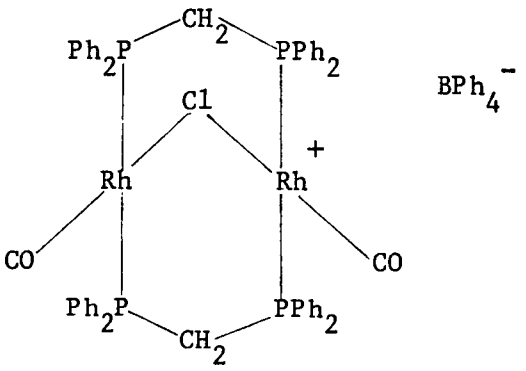


Figure 2. A representation of an A-Frame complex.

Complex 4 (p 6) would thus be considered an A-Frame complex in which the active site has been occupied.

A closely related system of A-Frame rhodium complexes which has been examined in more depth than complexes 3 (p 6) and 4 (p 6) consists of 5, $[Rh_2(CO)_2Cl(dpm)_2][BPh_4]$, and its CO derivative 6 which is the BPh_4^- analog of 4 (p 6).



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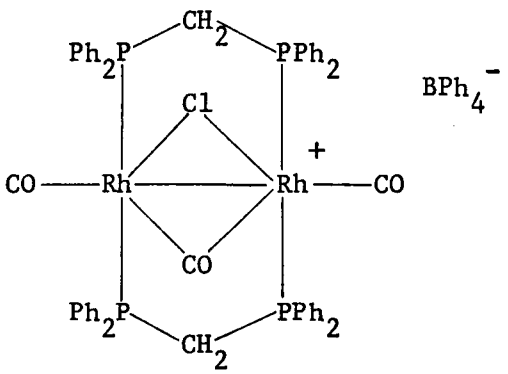
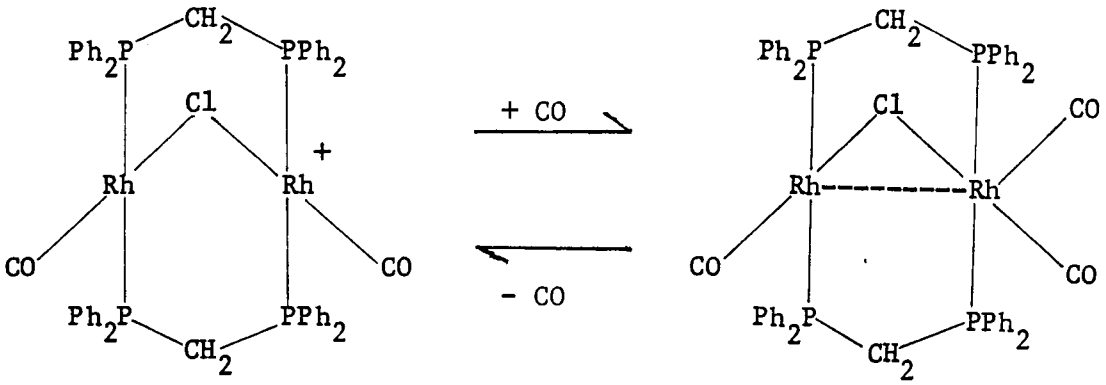


6

With the aid of ^{13}CO labelling and ^{13}C NMR it has been postulated that the CO addition involves a bridge-terminal CO exchange (Equation 3, p 9).[8]



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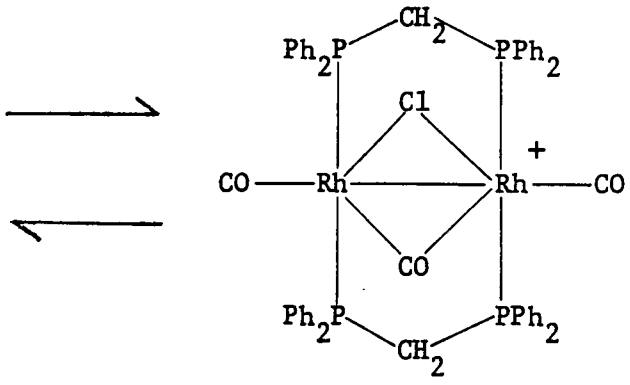
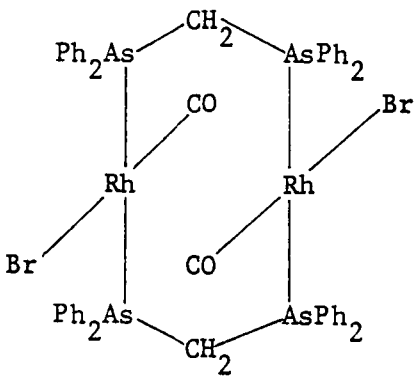


6

(3)

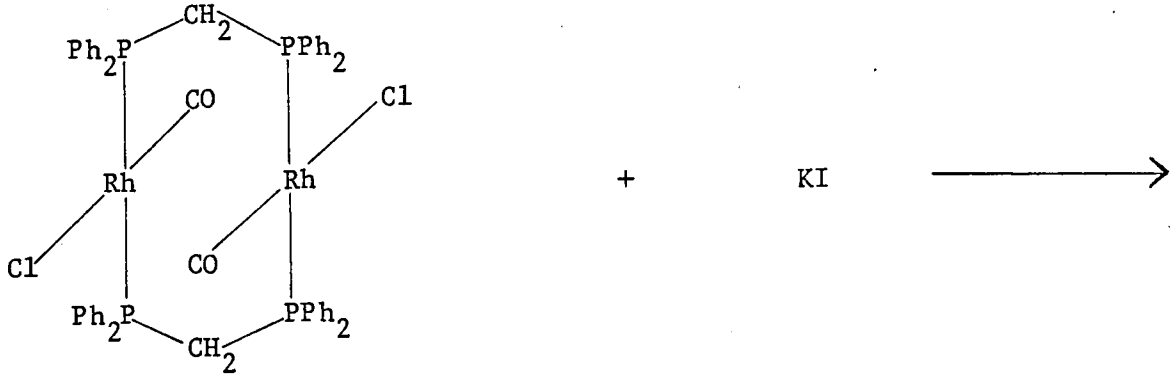
The only other halide complex which has the same structure as complexes 1 (p 5) and 2 (p 5) and has been isolated in a pure state is complex 7, the bromide (Br^-) analog of 2 (p 5).



7

The tendency of 7 (p 9) to undergo exchange reactions similar to those of 1 (p 5) and 2 (p 5) has not been investigated.

Both complexes 1 (p 5) and 2 (p 5) undergo halide exchange, but the new halide complexes formed do not have the structures exhibited by 1 (p 5), 2 (p 5), and 7 (p 9), (Equations 4,5,6).[5]



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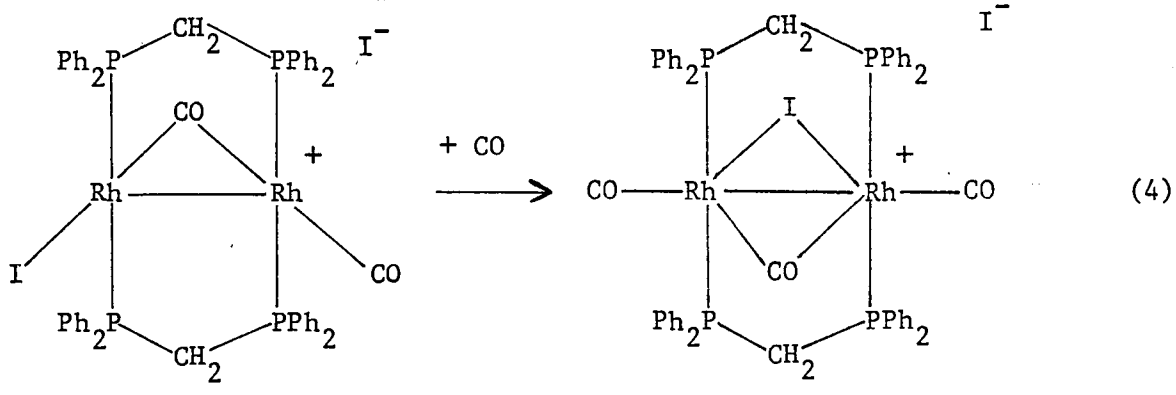
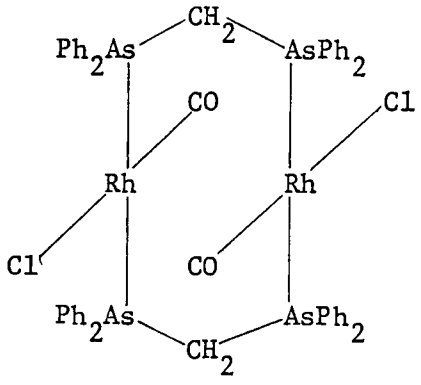
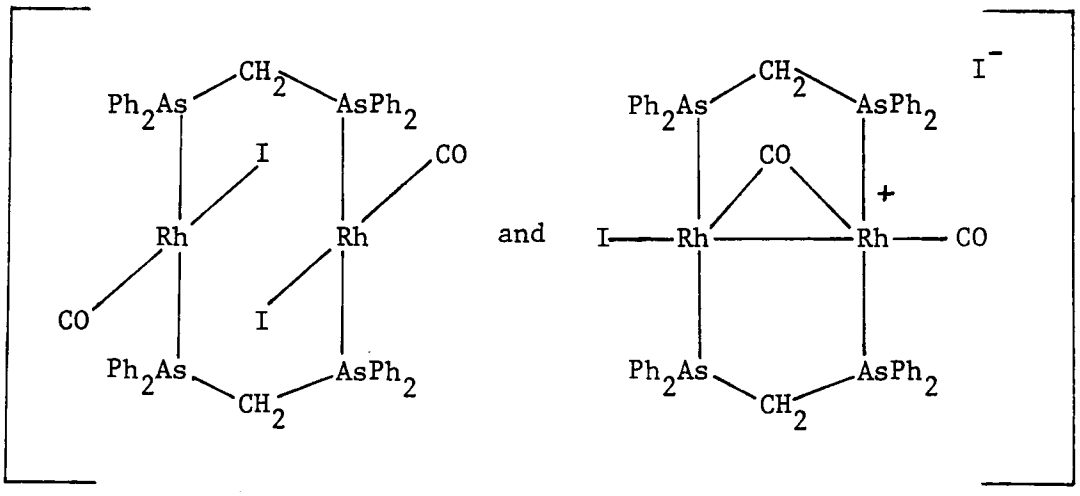


(4)

8 9

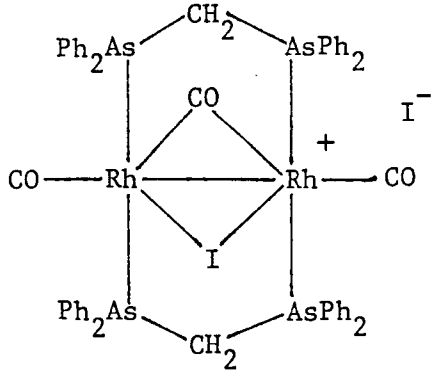


2 + KI ⟶

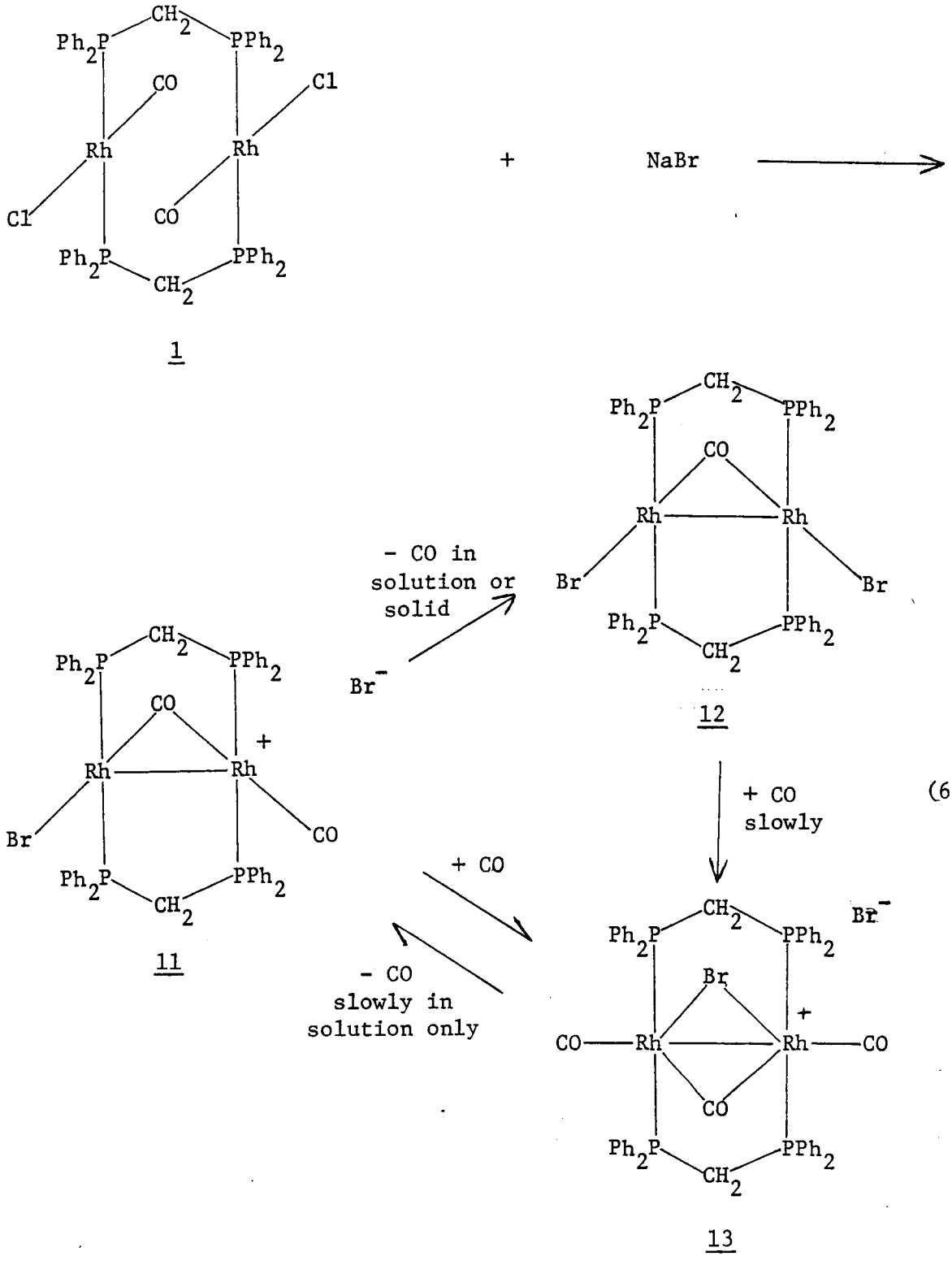


and

+ CO ⟶



10 (5)

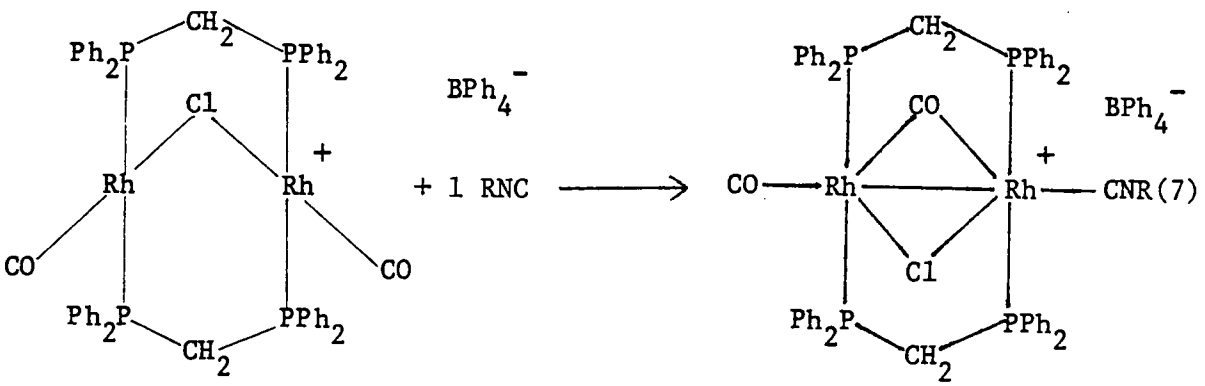


The fact that the RNC ligand is a better σ donor than CO but is involved in the same type of bonding mechanism makes the electrochemistry of rhodium complexes containing this ligand of interest. The majority of

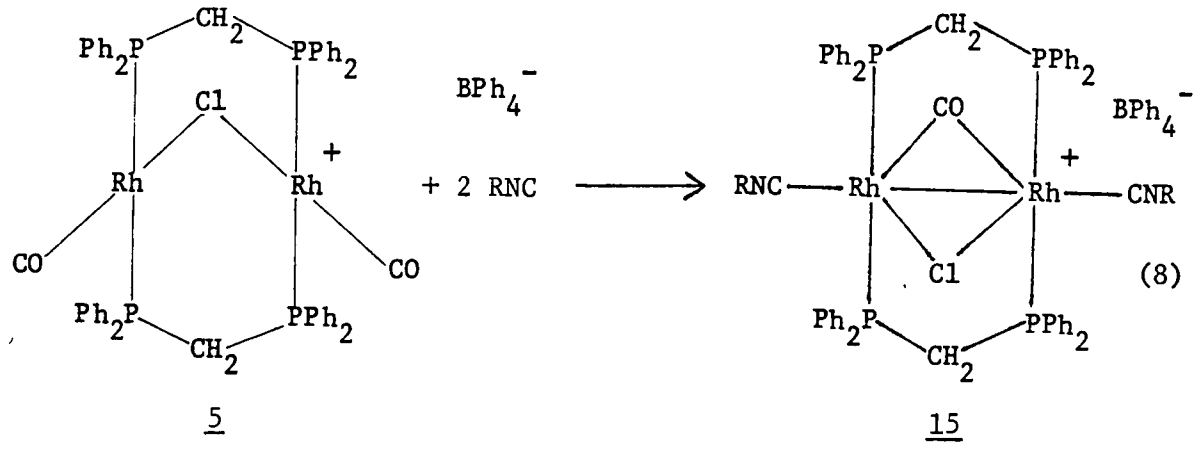
the research involving the electrochemistry of rhodium complexes containing RNC ligands is presently being conducted by other members of the research group. However, some complexes containing both RNC and CO ligands are pertinent to this study.

It is possible to synthesize $[Rh_2(RNC)_4(dpm)_2][PF_6]_2$ by removing two RNC ligands from $[Rh(RNC)_4][PF_6]$ upon adding dpm; however, this synthetic route cannot be used with dam because the dam will not replace the RNC ligands.[11] This suggests that dam is a weaker σ-donor than dpm and RNC.[7] This fact would partially explain the vast chemical differences between the dpm and dam complexes. Since dam is a weaker σ-donor, in a situation where other parameters such as steric hinderances and oxidation state are the same, the dam complexes should have less electron density at the metal. This difference in electron density at the metal would lead to different stabilities for analogous dam and dpm complexes. The difference in the electron density might also account for the different ways that ligands such as CO and RNC bind in the dpm and dam complexes.

The RNC complexes of interest in this thesis are made by the substitution of RNC for CO on complex 5 (p 8). Addition of one equivalent of RNC to 5 (p 8) gives complex 14 (Equation 7). When two equivalents of RNC are added to 5 (p 8), complex 15 is formed (Equation 8, p 14).[12]

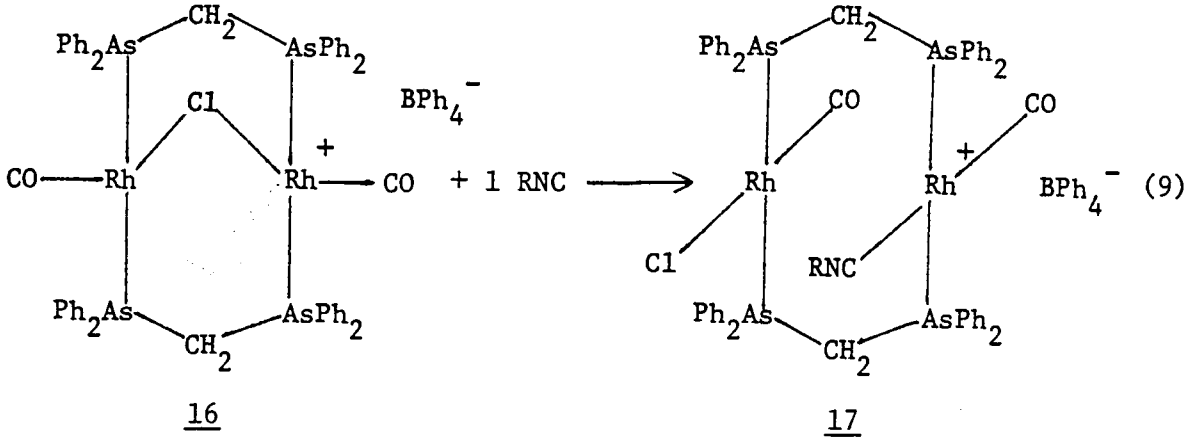


5 14

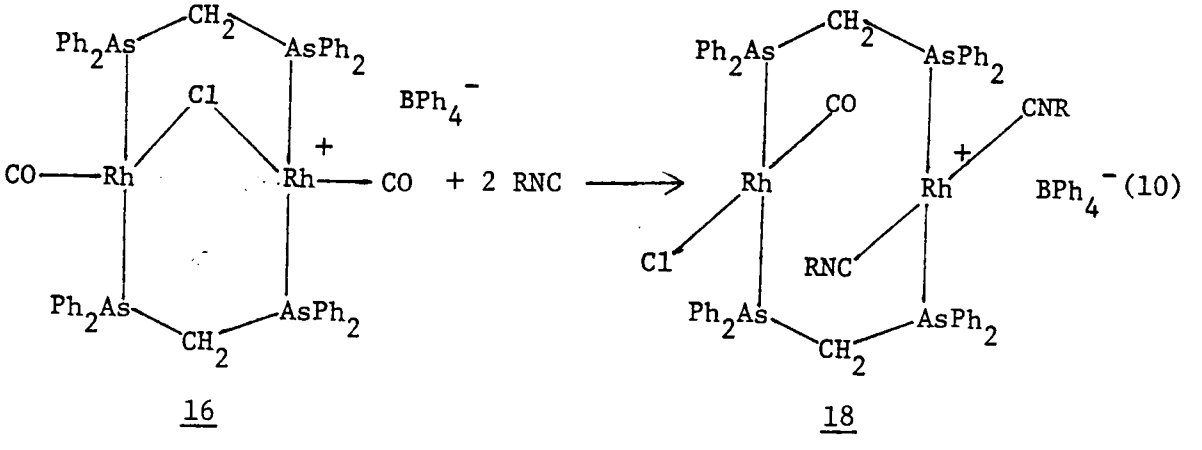


5 15

To illustrate another difference in the behavior of analogous dpm and dam complexes, when one equivalent of RNC is added to complex 16, the analog to 5 (p 8), complex 17 is obtained (Equation 9). Two equivalents of RNC give complex 18 (Equation 10).



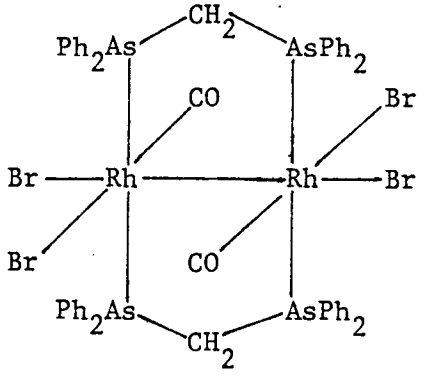
16 17



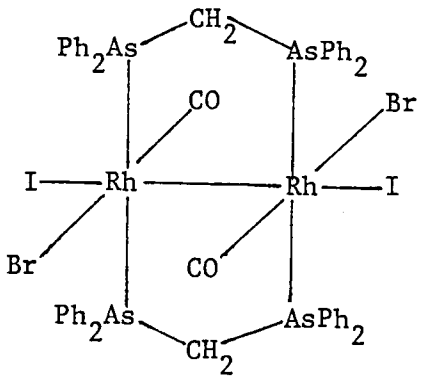
16 18

The diarsine complexes 17 (p 14) and 18 (p 14) contain no rhodium-rhodium bond and no bridging ligands other than the dam.[12]

The electrochemistry of the Rh(I) dimers focussed on in this study has not been previously investigated. Ther are, however, a few reported studies involving the chemical oxidation and reduction of some of these systems. For example, complex 7 (p 9) has been shown to undergo chemical oxidation with bromine and iodine to produce complexes 19a and 19b respectively. Complexes 19a and 19b have been characterized using IR and UV-Visible spectroscopies.[11]



19a

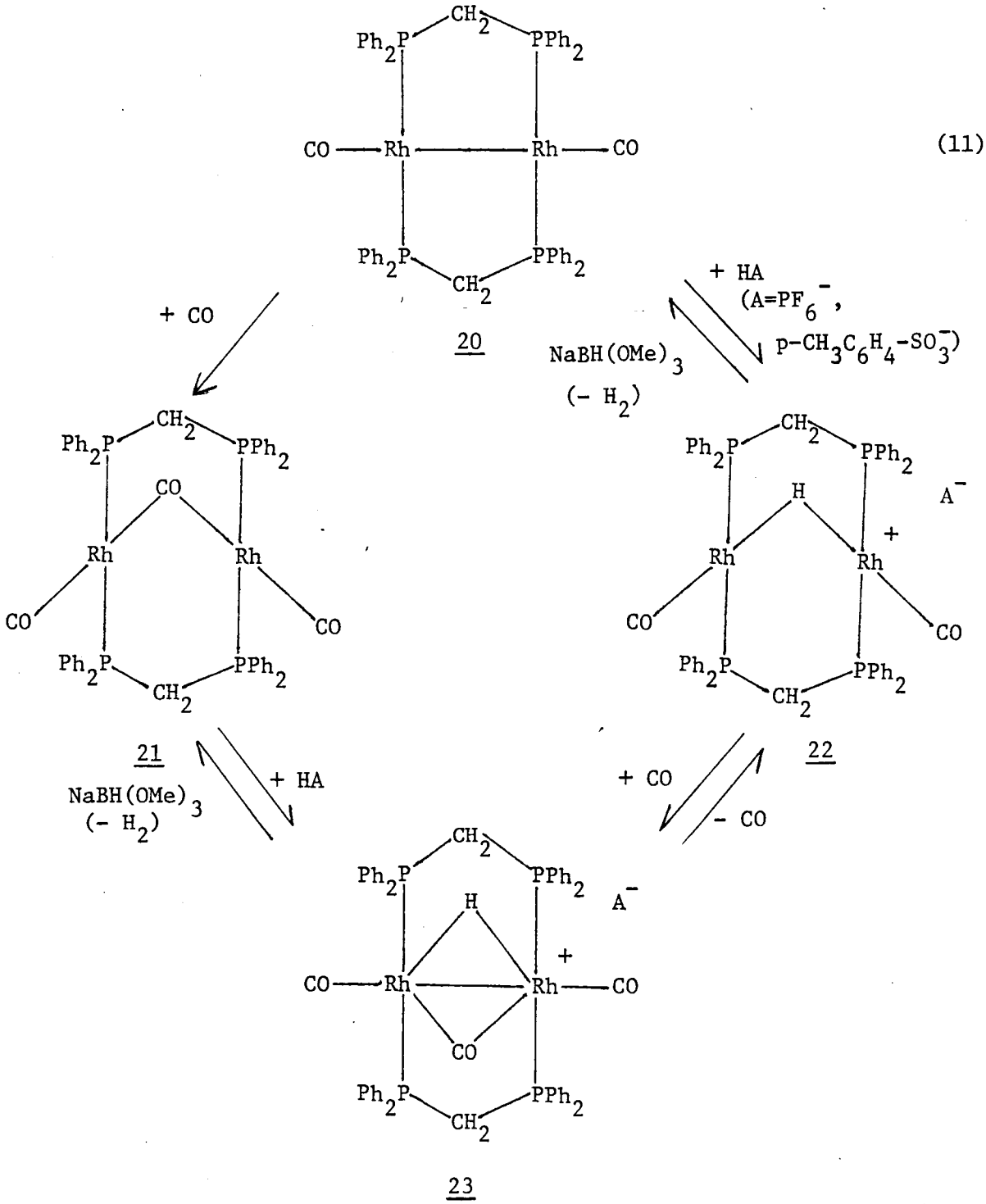


19b

The chemical reduction of 1 (p 5) with $NaBH_4$ has also been recently investigated.[13] The product of this reduction is a perfect example of the ability of CO to stabilize low oxidation states. Even though the complex which is isolated is the highly reactive Rh(0) dimer 20, it readily reacts with CO to form the A-Frame complex 21, Equation 11 (p 16). The Rh(0) dimer 20 also reacts with a proton (H^+) to form the dimer 22. However, on the basis of a ^1H NMR resonance at -10.1 ppm (TMS reference), complex 22 is considered to be a hydride bridged Rh(I) dimer instead of a Rh(0) dimer.

The purpose of this work is to investigate the electrochemical behavior of some carbonyl-containing rhodium complexes. The electrochemical

data could help explain some of the differences observed as a result of changing the ligands. It is also the goal of this study to isolate and characterize new rhodium complexes which might not be accessible by chemical means.



(11)

CHAPTER II

EXPERIMENTAL

A. Chemicals

1. Solvents

a. Methylene Chloride, (CH_2Cl_2). Spectroanalyzed CH_2Cl_2 (Fisher Scientific) was used without further purification.

b. Acetone. Certified ACS acetone (Fisher Scientific) was used without further purification.

c. Diethyl Ether, (ether). Certified ACS anhydrous ether (Fisher Scientific) was used without further purification.

d. Benzene. Certified ACS benzene (Fisher Scientific) was used without further purification.

e. Methanol. Certified ACS methanol (Fisher Scientific) was used without further purification.

f. Chloroform. Certified ACS chloroform (Fisher Scientific) was used without further purification.

g. Absolute Ethanol, (ethanol). Certified ACS ethanol (Aaper Alcohol) was used without further purification.

h. Ligroin. Certified ACS 30-60 ligroin (Fisher Scientific) was used without further purification.

i. Doubly-Distilled Water, (water). Water from the departmental still was redistilled using a WS-2 Continuous Water Still (Kontes Glass Company).

2. Reagents

a. Tetrabutylammonium Chloride, (TBACl). Reagent grade TBACl (Aldrich) was recrystallized three times from acetone and ether as outlined by Bard.[15]

b. Carbon Monoxide, (CO). CP grade CO (Air Products) was used without further purification.

c. Tetrabutylammonium Iodide, (TBAI). Reagent grade TBAI (Aldrich) was used without further purification to make other tetrabutylammonium salts.

d. Ammonium Hexafluorophosphate, (NH_4PF_6). Reagent grade NH_4PF_6 (Aldrich) or (Alfa) was used without further purification.

e. Tetrabutylammonium Hydroxide, (TBAOH). An aqueous 40% by weight solution of TBAOH (Aldrich) was used as purchased.

f. Hydrogen Hexafluorophosphate, (HPF_6). A 60% by volume aqueous solution of HPF_6 (Alfa) was used as purchased.

g. Tetracarbonyl-μ-dichlorodirhodium, ($Rh_2(CO)_4Cl_2$). Reagent grade $Rh_2(CO)_4Cl_2$ (Aldrich) or (Strem) was used without further purification.

h. Bis(diphenylphosphino)methane, (dpm). Reagent grade dpm (Strem) was used without further purification.

i. Bis(diphenylarsino)methane, (dam). Reagent grade dam (Strem) was used without further purification.

j. Hydrochloric Acid, (HCl). Solutions of HCl were prepared from certified ACS reagent grade HCl (Fisher Scientific).

k. Hydrobromic Acid, (HBr). Solutions of HBr were prepared from certified ACS reagent grade HBr (Fisher Scientific).

l. Tetrabutylisocyanide, (t-C_4H_9NC). Reagent grade t-C_4H_9NC (Aldrich) was used without further purification.

m. Nitric Acid, (HNO_3). Solutions of HNO_3 were prepared from certified ACS reagent grade HNO_3 (Fisher Scientific).

n. Rhodium(III) Trichloride Trihydrate, ($RhCl_3 \cdot 3H_2O$). Reagent grade $RhCl_3 \cdot 3H_2O$ (Strem) was used without further purification.

3. Supporting Electrolytes

a. Tetrabutylammonium Hexafluorophosphate, (TBAH). Metathesis of TBAI with NH_4PF_6 was originally used to prepare TBAH. Later, TBAH was prepared by the neutralization of TBAOH with HPF_6. The TBAH was recrystallized three times from acetone-water.

b. Tetrabutylammonium Bromide, (TBABr). Reagent grade TBABr (Aldrich) was recrystallized three times from a 1:10 mixture of acetone and ether.[14]

4. Miscellaneous

a. Argon, (Ar). Prepurified Ar (Selox, Inc.) was used without further purification.

b. Nitrogen, (N_2). Prepurified N_2 (Selox, Inc.) was used without further purification.

c. Sodium Metal, (Na). Reagent grade Na (Fisher Scientific) was used as received.

d. Nujol. High quality Nujol (Plough, Inc.) was used after drying over Na.

e. Phosphorus Pentaoxide, (P_2O_5). Certified ACS P_2O_5 (Fisher Scientific) was used without further purification.

B. Cyclic Voltammetry

1. Electrochemical Cell

A conventional one compartment cell fitted with a porous bottom was used for all voltammetry. For degassing, Ar was passed through the frit bottom and then allowed to flow over the solution while the voltammograms were being obtained.

2. Electrodes

A saturated calomel electrode (SCE) of standard design was used as a reference electrode. The SCE was always separated from the bulk solution

by a fine frit. The working electrode was a 0.24 cm^2 platinum button electrode (Beckman). A 2.76 cm^2 platinum grid was used as the counter electrode.

3. Instrumentation

a. Potentiostat. Early voltammetry was performed on a potentiostat built by the UT Chemistry Department Electronic Shop. The design was a modified version of that reported by Lodmell.[15] Later voltammetry was performed with a PAR 364 Polarographic Analyzer.

b. Sine Wave Generator. The potentiostats were used in conjuncture with a sine wave generator designed by Woodward and coworkers.[16] The generator was built by the UT Chemistry Department Electronic Shop.

c. Recorder. All voltammograms were recorded using a Houston Instruments 2000 Omnigraphic X-Y Recorder.

4. Solvent and Supporting Electrolytes

Methylene chloride was the only solvent used for voltammetry. Depending on the purpose, either TBAH or TBABr was used as the supporting electrolyte. The concentration of the supporting electrolyte was always 0.10 molar.

5. Coordinating Ligands

a. Carbon Monoxide. In the cases where CO could add to the complex either before or after electron transfer, the CO was used to degas the solution and to flow over the solution during the voltammetry.

b. Halides. Both TBACl or TBABr were added in a 10 fold molar excess when the respective halide ions were being used as coordinating ligands during voltammetry.

C. Coulometry

1. Electrochemical Cell

A conventional, H-shaped, three compartment cell was used for all coulometry. One compartment was fitted with a porous glass frit bottom

used for degassing and stirring the solution. The three compartments were separated by fine glass frits.

2. Electrodes

A SCE of standard design was used as a reference electrode. The SCE was always separated from the bulk solution by a fine frit. The working electrode was a 25 cm^2 platinum grid. A carbon rod electrode was used as the isolated counter electrode.

3. Coulometer

The early coulometric experiments were performed on an ORNL Electronic Controlled-Potential Coulometric Titrator, model Q-2005. A PAR 173 Potentiostat / Galvanostat equipped with a PAR 179 Digital Coulometer was used for later experiments.

4. Solvents and Supporting Electrolytes

The solvent systems used in voltammetry were also used for coulometry. The supporting electrolyte concentrations ranged from 0.10 to 0.20 molar.

5. Coordinating Ligands

The same coordinating ligands used in voltammetry were also used in coulometry. The halide salts, however, were added in 25 fold molar excess instead of 10 fold molar excess.

D. Spectroscopy

1. Infrared Spectroscopy

Infrared spectroscopy (IR) was carried out using a Digilab FTS-20 C/V Fourier Transform Infrared Spectrometer. Solid samples were prepared by making a Nujol mull and sealing the mull between thin polyethylene sheets using a Clamco Super Sealer.

2. Ultraviolet-Visible Spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) was carried out using a Cary 17 Spectrophotometer. Quartz cells (Fischer Scientific) of 1.0 cm pathlength were used. Methylene chloride or chloroform was used to make solutions of known concentration. One cell containing the solution was placed in the sample beam while a matching cell containing only solvent was placed in the reference beam.

E. Elemental Analysis

All elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

F. Preparation of Rhodium Complexes

1. "trans"-Dicarbonyldichlorobis[μ-methylenebis[diphenylphosphine]-P:P']-dirhodium(I), $Rh_2(CO)_2Cl_2(dpm)_2$, 1 (p 5)

Method A of Mague and Mitchner[6] was used to prepare 1 (p 5). To 0.40 g of $Rh_2(CO)_4Cl_2$ dissolved in 20 mL of benzene was added 1.6 g of dpm dissolved in 20 mL of benzene. The cloud point was induced by adding ether. After 12 hours at -10°C, an orange product was filtered off and dried in vacuum. If further purification were needed 1 (p 5) was redissolved in CH_2Cl_2 and precipitated as above. The yield was 90-95%.

The IR spectrum of a Nujol mull shows ν_{CO} at 1971 cm^{-1} (s) (lit.[6]: 1976 cm^{-1} (s)). The UV-Vis spectrum obtained in CH_2Cl_2 shows peaks at 440 nm, 302 nm and 252 nm (lit.[11]: 417nm, 301 nm, and 255 nm).

2. "trans"-Dicarbonyldichlorobis[μ-methylenebis[diphenylarsine]-As:As']-dirhodium(I), $Rh_2(CO)_2Cl_2(dam)_2$, 2 (p 5)

The same synthetic procedure was used for 2 (p 5) as was used for 1 (p 5).[6] To 0.31 g of $Rh_2(CO)_4Cl_2$ dissolved in 15 mL of benzene was added 1.5 g of dam dissolved in 15 mL of benzene. The cloud point was induced

by adding ether. After 12 hours at -10°C a red-orange product was filtered off and dried in vacuum. The yield was 85-90%.

The IR spectrum of a Nujol mull shows ν_{CO} at 1962 cm^{-1} (s) (lit.[6]: 1965 cm^{-1} (s)). The UV-Vis spectrum of a CH_2Cl_2 solution shows peaks at 464 nm, 288 nm and 240 nm (lit.[11]: 466 nm, 292 nm and 240 nm).

3. μ-Carbonyldicarbonyl-μ-chlorobis[μ-methylenebis[diphenylphosphine]-P:P']-dirhodium(I)(Rh-Rh) Hexafluorophosphate, $[Rh_2(CO)_3Cl(dpm)_2][PF_6]$, 24

The procedure that Mague and Sanger[8] used to make the analogous BPh_4^- complex 6 (p 8) was used to prepare 24. A red-orange solution of 0.20 g of $RhCl_3 \cdot 3H_2O$ in 25 mL ethanol and 0.5 mL of water was refluxed for five hours while being bubbled with CO. The resulting lemon yellow solution was allowed to cool to room temperature and solutions of 0.27 g dpm in 3 mL of acetone and 0.11 g ammonium hexafluorophosphate in 3 mL of ethanol were added in rapid succession while maintaining the flow of CO. After the evolution of CO, the product which was precipitated as yellow crystals was then filtered. After being washed with water, ethanol, and ether, the complex was dried in vacuum. The yield was 70%.

The IR spectrum of a Nujol mull shows ν_{CO} at 2003 cm^{-1}(sh), 1982 cm^{-1} (s) and 1875 cm^{-1}(m) (lit.[8] for BPh_4^- salt: 1992 cm^{-1}, 1953 cm^{-1} and 1869 cm^{-1}).

4. Tetrabutylammonium Dicarbonyldichlororhodium(I), $[(C_4H_9)_4N][Rh(CO)_2(Cl)_2]$.

A procedure outlined by Vallarino[17] was used to prepare this complex. To a 10 mL methanol solution containing 1.5 mL concentrated HCl was added 0.30 g of $Rh_2(CO)_4Cl_2$. The resulting pale yellow solution was treated with 0.50 g of TBACl dissolved in 2.5 mL of methanol. The solution was reduced under vacuum until yellow crystals precipitated. The crystals were filtered and washed with 25 mL of 10% HCl. The yield was 65%.

5. Tetrabutylammonium Dibromodicarbonylrhodium(I), $[(C_4H_9)N][Rh(CO)_2(Br)_2]$

A procedure outlined by Vallarino[17] was used to prepare this complex. To 20 mL of ice cold methanol containing 3.0 mL HBr was added 0.50 g of $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$. This solution was quickly filtered and the volume was reduced under vacuum until yellow crystals precipitated. The yellow crystals were filtered and washed with cold water. The final complex was dried in vacuum and the yield was 60%.

An IR spectrum of a Nujol mull shows peaks at 2054 cm^{-1}, 1983 cm^{-1}, 606 cm^{-1}, 495 cm^{-1}, 483 cm^{-1}, and 449 cm^{-1} (lit.[17]: 2062 cm^{-1}, 1985 cm^{-1}, 604 cm^{-1}, 492 cm^{-1}, 481 cm^{-1}, and 446 cm^{-1}).

6. Dicarbonyl-μ-chlorobis[μ-[methylenebis[diphenylphosphine]-P:P']dirhodium(I) Hexafluorophosphate, $[Rh_2(CO)_2Cl(dpm)_2][PF_6]$, 25

The procedure that Mague and Sanger[8] used to make the analogous BPh_4^- complex 5 (p 8) was used to prepare 25. A yellow-orange solution of 1.2 g of 24 (p 23) in 25 mL acetone was bubbled with N_2 for 20 minutes. The orange solution was treated with 1:1 ether-ligroin until the cloud point was reached. The solution was then cooled for one hour. The bright yellow crystals were filtered and dried in vacuum. The yield was 45%.

The IR spectrum of a Nujol mull shows ν_{CO} at 1994 cm^{-1}(sh) and 1978 cm^{-1} (s) (lit.[8] for BPh_4^- salt: 1997 cm^{-1} and 1978 cm^{-1}).

7. "trans"-Dibromodicarbonylbis[μ-methylenebis[diphenylarsine]-As:As']-dirhodium, $Rh_2Br_2(CO)_2(dam)_2$, 7 (p 9)

Method D of Mague and Mitchner[6] was used to prepare 7 (p 9). To 0.25 g of dam dissolved in 8 mL of benzene was added 0.30 g of $[(C_4H_9)_4N][Rh(CO)_2Br_2]$ dissolved in 20 mL of absolute ethanol. The cloud point was induced in the red solution by adding ether. After 12 hours at -10°C a red-orange product was filtered off and dried in vacuum. The yield was 94%.

The IR spectrum of a Nujol mull shows ν_{CO} at 1969 cm^{-1}(s) and 1925 cm^{-1}(w) (lit.[6]: 1965 cm^{-1} and 1923 cm^{-1}). Anal. Calcd for $C_{52}H_{44}As_4Br_2O_2Rh_2$: Br,11.12. Found: Br,11.70.

8. μ-Carbonyl-μ-chlorobis[μ-methylenebis[diphenylphosphine]-P:P']bis(tetrabutylisocyanide)dirhodium(I) Hexafluorophosphate, $[Rh_2(CO)Cl(t\text{-}C_4H_9NC)_2(dpm)_2][PF_6]$, 26

This procedure is a modified version of that used by Mague and DeVries[12] to make the analogous BPh_4^- complex 15 (p 14). To 0.32 g of 25 (p 24) dissolved in 10 mL of acetone a solution of 0.047 g of $t\text{-}C_4H_9NC$ dissolved in 9 mL of acetone was added dropwise while stirring vigorously. The evolution of a gas (presumably of CO) was observed. The complex was precipitated with 1:1 ether-ligroin and the orange product was filtered. While still in the frit, 10 mL of acetone was stirred in and pulled through. The red solution which resulted was treated with 1:1 ether-ligroin and the complex precipitated. An IR spectrum showed a contaminant peak at 1964 cm^{-1}(w) so the complex was redissolved in 10 mL of acetone and 0.0055 g of $t\text{-}C_4H_9NC$ dissolved in 2 mL acetone was added dropwise. Upon precipitation with 1:1 ether-ligroin a pure product was recovered in a yield of 55%.

The IR spectrum of a Nujol mull shows ν_{RNC} at 2125 cm^{-1}(s) and ν_{CO} at 1813 cm^{-1}(m) (lit.[12] for the BPh_4^- salt: 2155 cm^{-1} and 1827 cm^{-1}). Anal. Calcd for $C_{61}H_{62}ClF_6N_2OP_5Rh_2$: C,54.30; H,4.63; N,2.08; Cl,2.63. Found: C,54.33; H,5.23; N,1.91; Cl,2.76.

9. μ-Carbonyl-μ-chlorodichlorobis[μ-methylenebis[diphenylphosphine]-P:P']-dirhodium(II) Hexafluorophosphate, $[Rh_2(CO)Cl_3(dpm)_2][PF_6]$, 27

An orange solution of 0.040 g of 1 (p 5) in 40 mL of CH_2Cl_2 which contained 0.20 molar TBAH and 0.10 g of TBACl was oxidized at +0.60 volts. The coulombs were recorded and indicated an apparent electron count of two (n=1.72). The dark orange solution which resulted from the electrolysis

was stripped to dryness on a rotary-evaporator. A portion of the residue was saved for IR analysis. The remainder of the residue was treated with 40 mL of methanol. The mixture turned dark green within five minutes. After stirring for 12 hours, complex 27 was filtered off, then washed with water and methanol. The green complex was dried under vacuum. The yield was 60%.

The IR spectrum of a Nujol mull shows ν_{CO} at 1802 cm^{-1} (s). The spectrum also shows PF_6^- peaks at 839 cm^{-1} (s) and 560 cm^{-1} (m). The UV-Vis spectrum shows peaks at 350 nm(ϵ, 13000), 304 nm(ϵ, 27000) and a large peak at around 250 nm($\epsilon \doteq 50000$). Anal. Calcd for $C_{51}H_{44}Cl_3F_6OP_5Rh_2$: C,48.85; H,3.54; Cl,8.48; P,12.35. Found: C,47.47; H,3.80; Cl,8.77; P,11.67. The IR spectrum (Nujol vs. TBAH) of the portion of the residue which was saved when the CH_2Cl_2 was removed shows ν_{CO} at 2024 cm^{-1} (w).

10. Dicarbonyl-μ-chlorodichlorobis[μ-methylenebis[diphenylarsine]-As:As']-dirhodium(II)(Rh-Rh) Hexafluorophosphate, $[Rh_2(CO)_2Cl_3(dam)_2][PF_6]$, 28

A red-orange solution of 0.051 g of 2 (p 5) in 40 mL of CH_2Cl_2 which contained 0.15 molar TBAH and 0.11 g of TBACl was oxidized at +0.65 volts. The coulombs were recorded and indicated an apparent electron count of two (n=2.04). The dark orange solution which resulted from the electrolysis was stripped to dryness on a rotary-evaporator. A portion of the residue was saved for IR analysis. The remainder of the residue was treated with 30 mL of methanol. After stirring for 12 hours, the fluffy orange product was filtered off, then washed several times with methanol and water. The complex after 12 hours of drying under vacuum appeared to be a brown-orange product. The yield was 20%.

The IR spectrum of a Nujol mull shows ν_{CO} at 1982 cm^{-1} (s) and 1992 cm^{-1} (sh-m). The spectrum also shows PF_6^- peaks at 839 cm^{-1} (vs) and 558

cm^{-1}(m). The UV-Vis spectrum shows a peak at 328 nm. Anal. Calcd for $C_{52}H_{44}As_4Cl_3F_6O_2PRh_2$: C,42.55; H,3.04; Cl,7.30. Found: C,42.86; H,3.45; Cl,8.72. The IR spectrum (Nujol vs. TBAH) of the portion of the residue which was saved when the CH_2Cl_2 was removed shows ν_{CO} at 1965 cm^{-1} (w) and 2045 cm^{-1} (w).

11. Tetrabromodicarbonylbis[μ-methylenebis[diphenylarsine]-As:As']dirhodium(II)(Rh-Rh), $Rh_2Br_4CO_2(dam)_2$, 19a (p 15)

A red-orange solution of 0.055 g of 7 (p 5) in 40 mL of CH_2Cl_2 which contained 0.15 molar TBAH and 0.32 g of TBABr was oxidized at +0.60 volts. The coulombs were recorded and indicated an apparent electron count of two (n=2.05). The red solution which resulted from the electrolysis was stripped to dryness on a rotary-evaporator. A portion of the residue was saved for IR analysis. The remainder of the residue was treated with 40 mL of methanol. After stirring for 12 hours the brown product was filtered off, then washed several times with methanol and water. The product was then dried under vacuum to yield a pale brown product. The yield was 60%.

The IR spectrum of a Nujol mull shows ν_{CO} at 2017 cm^{-1} (s) and 1998 cm^{-1} (sh-vw) (lit.[11]: 2024 cm^{-1} in chloroform). The UV-Vis spectrum obtained in chloroform shows peaks at 427 nm (ϵ, 17000), 333 nm (ϵ, 29000) and 257 nm (ϵ, 29000) (lit.[11]: 430 nm (ϵ, 23000), 348 nm (ϵ, 35000) and 260 nm (ϵ, 35000)). Anal. Calcd for $C_{52}H_{44}As_4Br_4O_2Rh_2$: C,40.93; H,2.91; Br, 20.95. Found: C, 40.73; H, 3.02; Br,23.65. The IR spectrum (Nujol vs. TBAH) of the portion of the residue which was saved when the CH_2Cl_2 was removed shows ν_{CO} at 2017 cm^{-1} (m).

12. μ-Chlorodichlorobis[μ-methylenebis[diphenylphosphine]-P:P']bis[tetrabutylisocyanide]dirhodium(II) Hexafluorophosphate, $[Rh_2Cl_3(t\text{-}C_4H_9NC)_2(dpm)_2][PF_6]$, 29

A dark orange solution of 0.050 g of 26 (p 25) in 40 mL of CH_2Cl_2 which contained 0.20 molar TBAH and 0.10 g of TBACl was oxidized at +0.60 volts. The coulombs were recorded and indicated an apparent electron count of two (n=1.95). The dark red solution was evaporated to dryness on a rotary-evaporator. The red-orange residue was treated with 40 mL of methanol and stirred for 12 hours. The red complex which did not dissolve in the methanol was filtered and dried in vacuum. The yield was 50%.

The IR spectrum of a Nujol mull shows ν_{RNC} at 2225 cm^{-1}(w) and 2176 cm^{-1}(s). The PF_6^- peaks were observed at 839 cm^{-1}(s) and 558 cm^{-1}(m). The UV-Vis spectrum shows peaks at 372 nm(ϵ, 12000), 301 nm(ϵ, 8800), 279 nm(ϵ, 10000) and 267 nm(ϵ, 11000). Anal. Calcd for $C_{60}H_{62}Cl_3F_6P_5Rh_2$: C, 51.77; H,4.49; N,2.01; Cl,7.64. Found: C,49.81; H,4.69; N,1.94; Cl,7.56.

13. μ-Bromodicarbonyl-μ-hydride[μ-methylenebis[diphenylphosphine]-P:P'] dirhodium(I) Trihydrate, $Rh_2Br(CO)_2H(dpm)_2 \cdot 3H_2O$, 30

An orange solution of 0.040 g of 1 (p 5) in 40 mL of CH_2Cl_2 which contained 0.15 molar TBABr was reduced at -1.45 volts while being stirred with CO. The coulombs were recorded and indicated an apparent electron count of two (n=1.86). The brown-orange solution which resulted from the electrolysis was stripped to dryness on a rotary-evaporator. The residue was treated with 50 mL of water. After stirring for two hours a pale brown product was filtered off, then washed with water. The product was found to be soluble in ether, so it could not be rinsed with ether and had to be dried in vacuum for 12 hours in the presence of P_2O_5. The yield was 80%.

The IR spectrum of a Nujol mull shows ν_{CO} at 1958 cm^{-1}(s) and 1937 cm^{-1}(sh-m). Anal Calcd for $C_{52}H_{51}BrO_5P_4Rh_2$: C,53.58; H,4.41; Br, 6.85. Found: C,54.57; H,5.13; Br,6.24.

CHAPTER III

RESULTS AND DISCUSSION

In order to compare the electrochemical behavior of complexes 1 (p 5) and 2 (p 5), it was necessary to perform the electrochemistry under the same conditions. The insolubility of 1 (p 5) in most solvents limited the number of systems in which complexes 1 (p 5) and 2 (p 5) could be examined. It was found, however, that a $5x10^{-4}$ M concentration of both complexes could be prepared in CH_2Cl_2. For this reason, the system which was used for all initial voltammetry was CH_2Cl_2 containing the noncoordinating supporting electrolyte TBAH.

Figure 3 (p 30) shows the cyclic voltammogram of 1 (p 5) in CH_2Cl_2 and TBAH. The only well defined redox couple was the reduction (R1) at -1.43 volts and its corresponding oxidation (Ox1) at -0.22 volts. Due to a large reduction wave near the solvent limit an electron count was not obtained. The reduction waves at -0.16 volts (R2) and -0.80 volts (R3) appear to be primarily associated with the oxidation wave (Ox2) near +0.47 volts. It cannot be stated with certainty that R2 and R3 are not also associated with the oxidation waves at +1.10 volts (Ox3) and +1.27 volts (Ox4) since sweeping through Ox3 and Ox4 tends to increase the peak currents of R2 and R3. The ill defined behavior of complex 1 (p 5) during oxidation can probably be attributed to the ineffectiveness of the coordinated ligands to stabilize the higher oxidation states. In an attempt to stabilize these higher oxidation states of complex 1 (p 5), 10-fold molar excess of free chloride (Cl^-) was introduced into the system as TBACl. The voltammogram (Figure 4A, p 31) of this solution showed a much more pronounced oxidation wave (Ox2) at +0.40 volts. Figure 4A (p 31) is similar to

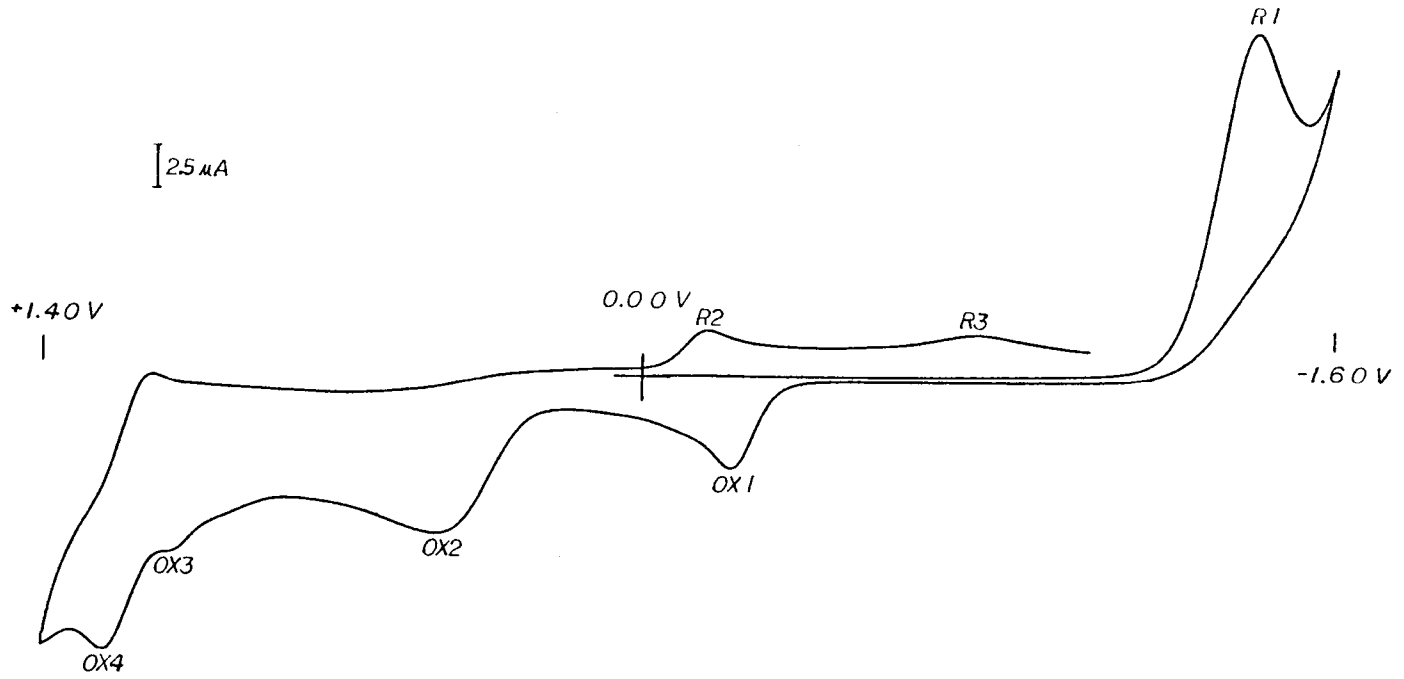


Figure 3. Cyclic voltammogram of 1.

Conditions: Conc. 5.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 50 mV sec^{-1}; SCE.

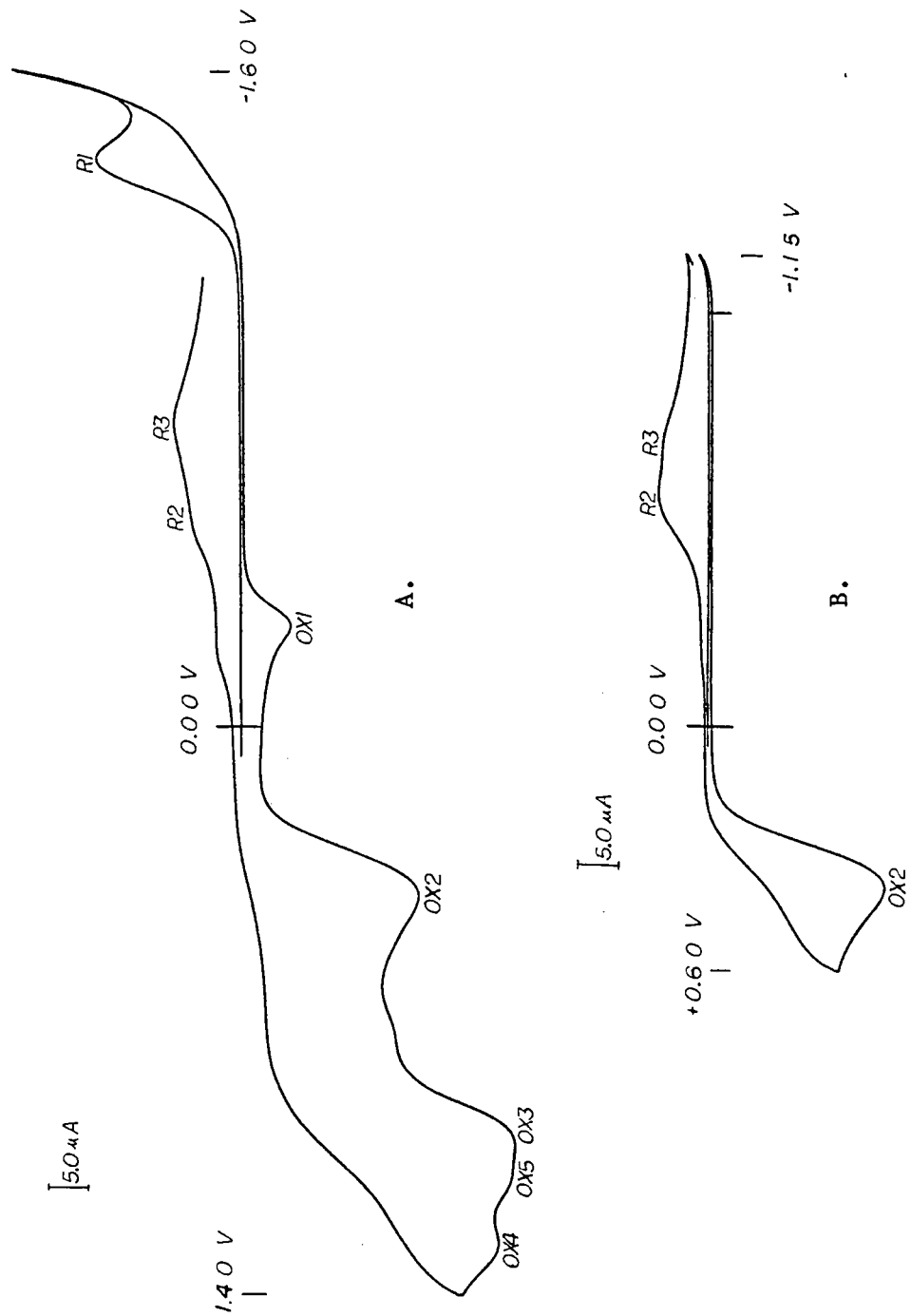


Figure 4. Cyclic voltammagram of 1 with excess TBACl.

Conditions A and B: Conc. 5.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 50 mV sec^{-1}; SCE.

Figure 3 (p 30) except for the oxidation (Ox5) at +1.10 volts which is apparently due to free Cl^-.[18] Ox2 has been further isolated in Figure 4B (p 31) clearly showing that the reduction (R2) at -0.50 volts and the reduction (R3) at -0.75 volts are associated with Ox2.

Using exhaustive coulometry at +0.60 volts, Ox2 of Figure 4B (p 31) dissappears resulting in the voltammogram shown in Figure 5 (p 33). Coulometry indicates that this oxidation is an apparent two-electron process, the product of which gives a reduction wave (R1) at -0.82 volts. The CH_2Cl_2 was stripped off the solution and an IR spectrum of the resulting residue (TBAH, TBACl and an unknown rhodium complex) shows only one ν_{CO} peak at 2024 cm^{-1} (w). This peak is indicative of at least one terminal CO in the complex. If two CO ligands remain on the oxidized product it is reasonable to expect that reduction of the oxidized solution would generate the original complex. If a CO is lost during the oxidation, bubbling the solution with Ar during the electrolysis should dispel the CO and make it impossible to return to the original species which contains two CO ligands. Thus in order to determine the number of terminal carbonyls a second solution was oxidized under the same conditions but at the end of the oxidation the solution was reduced at -1.30 volts. The coulometry suggests a two-electron reduction. The voltammogram of this reduced solution (Figure 6, p 34) was not the same as that shown in Figure 4B (p 31). This would suggest that during the oxidation process one CO was displaced thus preventing the oxidation product from returning to the original complex.

The unknown rhodium complex was isolated by treating the residue with methanol to remove the TBAH and TBACl. The IR spectrum of the isolated product shows a single peak for ν_{CO} at 1802 cm^{-1} (s) which is indicative of a bridging CO. The elemental analysis is consistent with the formula

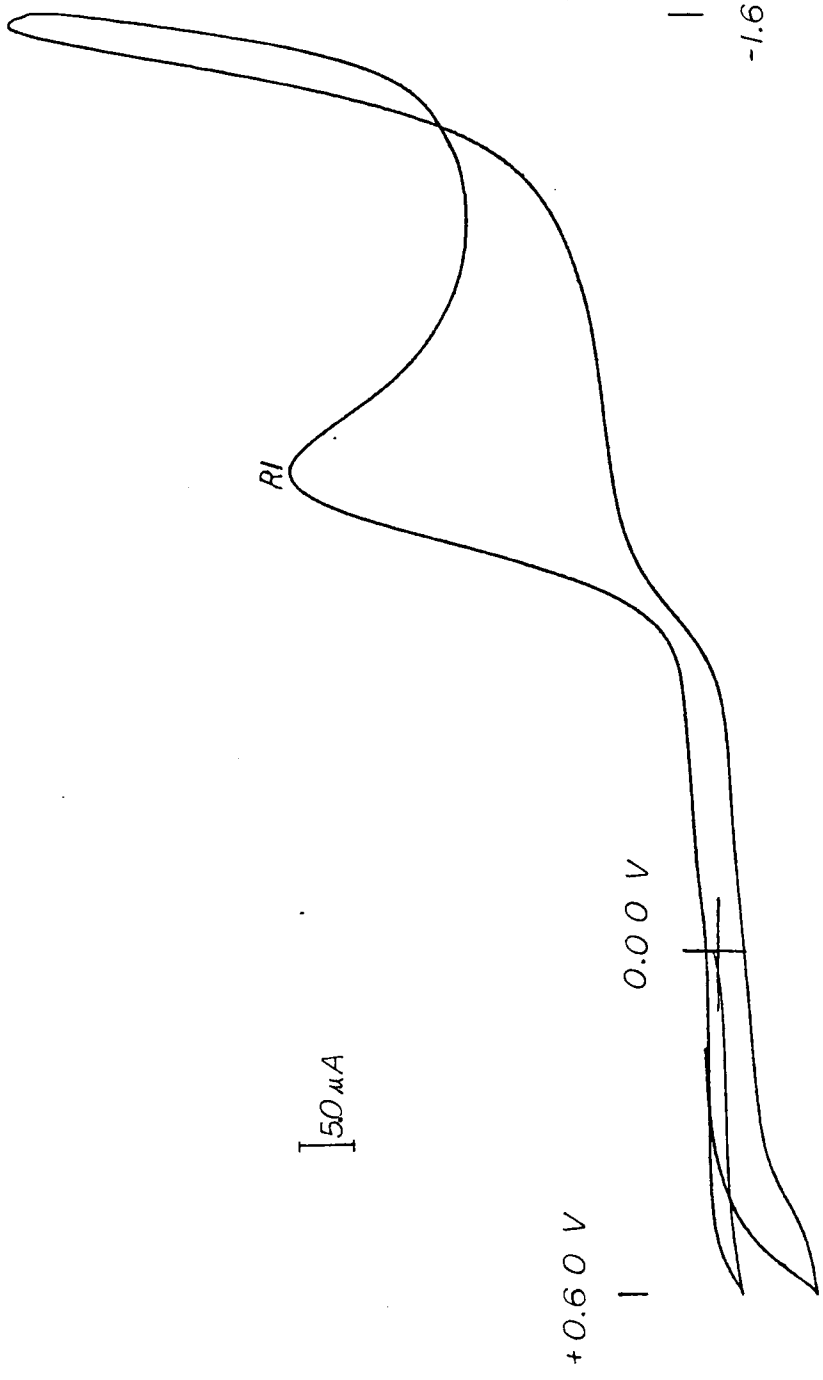


Figure 5. Cyclic voltammogram of 1 with excess TBACl after oxidation at +0.60 volts.

Conditions: Conc. 9.1×10^{-4} M; 0.20 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

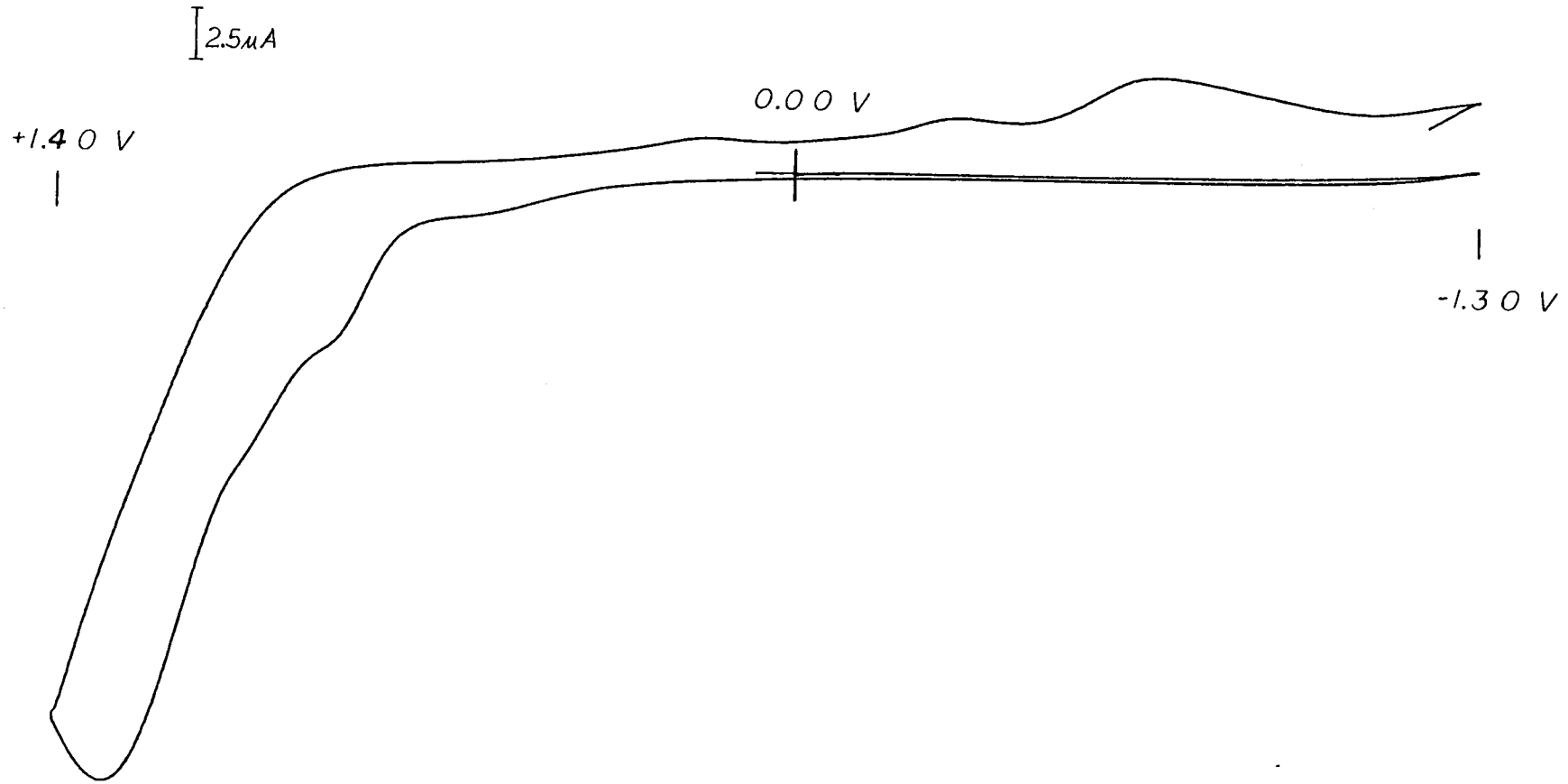
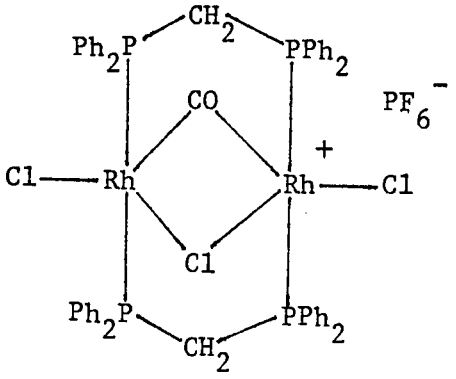


Figure 6. Cyclic voltammogram of 1 with excess TBACl after oxidation at +0.60 volts followed by reduction at -1.30 volts.

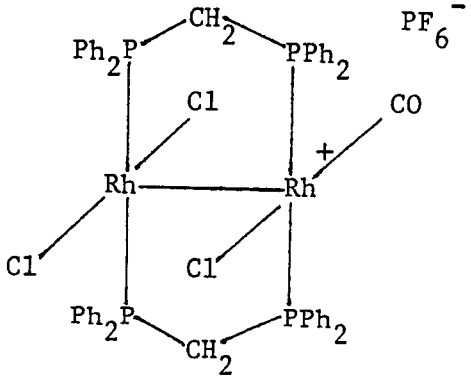
Conditions: Conc. 5.0×10^{-4} M; 0.20 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

$[Rh_2(CO)Cl_3(dpm)_2][PF_6]$ (27, p 25). Since many dpm dimers seem to prefer to exist as symmetric complexes, one of the Cl^- in 27 (p 25) is considered to be a bridging Cl^-.



27

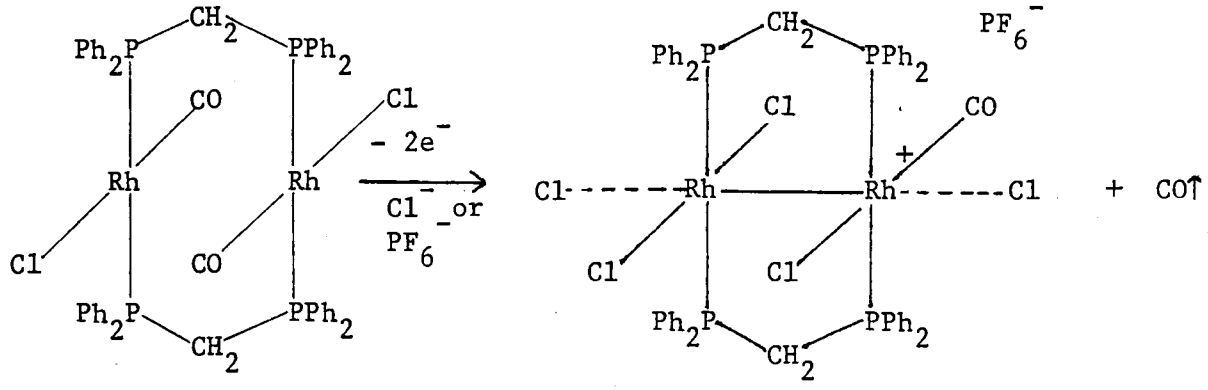
Based on the proposed structure of 27 (p 25) and the presence of only one terminal CO on the unknown rhodium complex in the residue from the oxidized solution, the unknown complex can be reasonably formulated as 31.



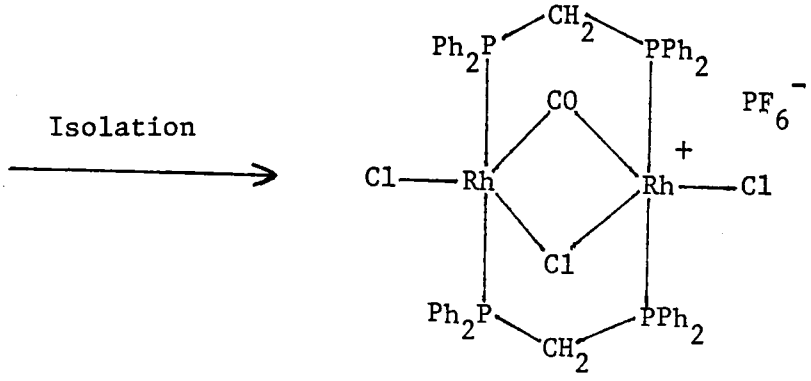
31

It appears that complex 31 cannot adopt the structure of complex 27 (p 25) until the removal of the excess Cl^- and PF_6^-. It is possible that weak association of these anions to the rhodium-containing cation is occurring along the rhodium-rhodium bond axis, preventing the cation from collapsing to the bridged species 27 (p 25). Equation 12 represents the

reaction in its entirety.



1 31



27

The presence of a strong σ-donor like Cl^- leads to stabilization of the oxidation product of complex 1 (p 5) to such an extent that a stable Rh(II) dimer is isolated. Conversely, a strong π-acceptor ligand should stabilize the reduction product of complex 1 (p 5).

When CO is bubbled through a solution of complex 1 (p 5), the complex is converted to complex 4 (p 6) (Equation 1, p 6). The voltammogram of 4 (p 6)(Figure 7, p 37) in the presence of free CO is much simpler than that for complex 1 (p 5) (Figure 3, p 30). The reduction wave (R1)(Figure 7, p 37) at -1.39 volts shows a corresponding oxidation wave (Ox1) at -0.16

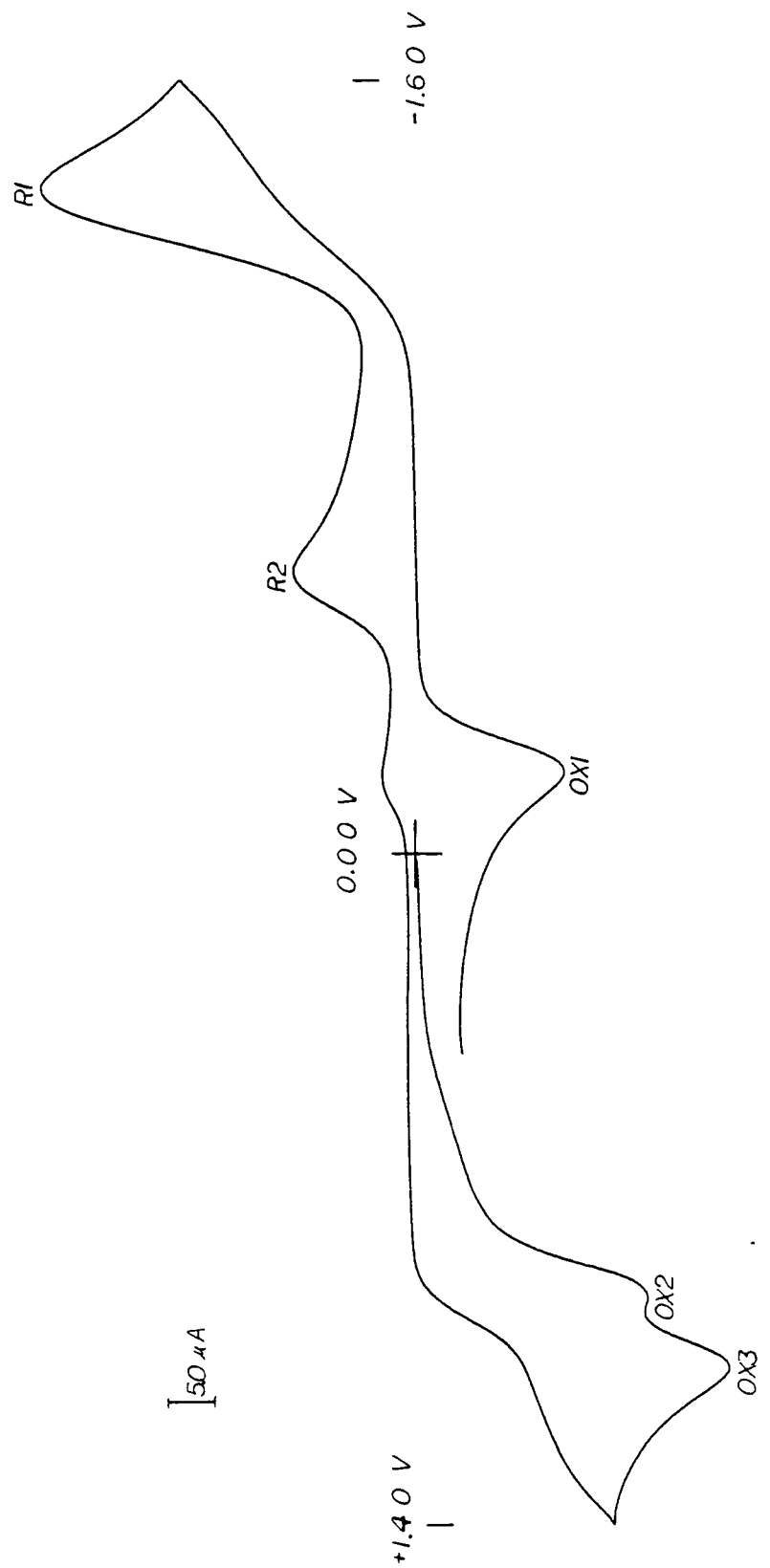


Figure 7. Cyclic voltammogram of 1 with excess CO.

Conditions: Conc. 5.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

volts. The oxidation (Ox3) at +1.07 volts is possibly due to the free Cl^- which is produced when 1 (p 5) is converted to 4 (p 6). In order to verify this, excess Cl^- was added to the system and Ox3 grew enormously (Figure 8, p 39). A new redox couple (R3/Ox4) also appeared which can be explained if it is assumed that there is a weak association between complex 4 (p 6) and the excess Cl^-. This associated species might then undergo oxidation accompanied by the loss of CO to give complex 31 (p 35), evidenced by the reduction wave (R3) appearing at -0.82 volts.

Since Ox2 of Figure 7 (p 37) is the only oxidation associated with the Rh(I) cationic dimer of complex 4 (p 6), a good electron count on Ox2 was desired. Complex 24 (p 23) was examined for this purpose because it has the same cation but an electroinactive anion which would not interfere with exhaustive coulometry as does Cl^-. Figure 9 (p 40) shows that 24 (p 23) does indeed retain the R1/Ox1 couple while only showing the one oxidation (Ox2) at +1.06 volts. The electron count could not be obtained for Ox2 due to the generation of another electroactive species. Comparison of Figures 7 (p 37) and 9 (p 40) indicates that the lack of a free Cl^- in a solution of 24 (p 23) does seem to alter the nature of the oxidation products. However, the products could not be identified in either case.

In an attempt to prepare a Rh(0) dimer, complex 1 (p 5) was coulometrically reduced at -1.45 volts while being bubbled with CO. Due to the solubility of TBABr in water the electrolysis system was changed to CH_2Cl_2 and TBABr so the eventual separation of the residue (TBABr and a rhodium complex) could be easily accomplished. As seen by comparing Figure 10A (p 41) and Figure 7 (p 37) the use of TBABr as the supporting electrolyte does not affect the redox couple (R1/Ox1) which appears when 1 (p 5) is bubbled with CO in the TBAH system. The exhaustive coulometry produced a voltammogram (Figure 10B, p 41) with the one oxidation wave (Ox1) at -0.06 volts while

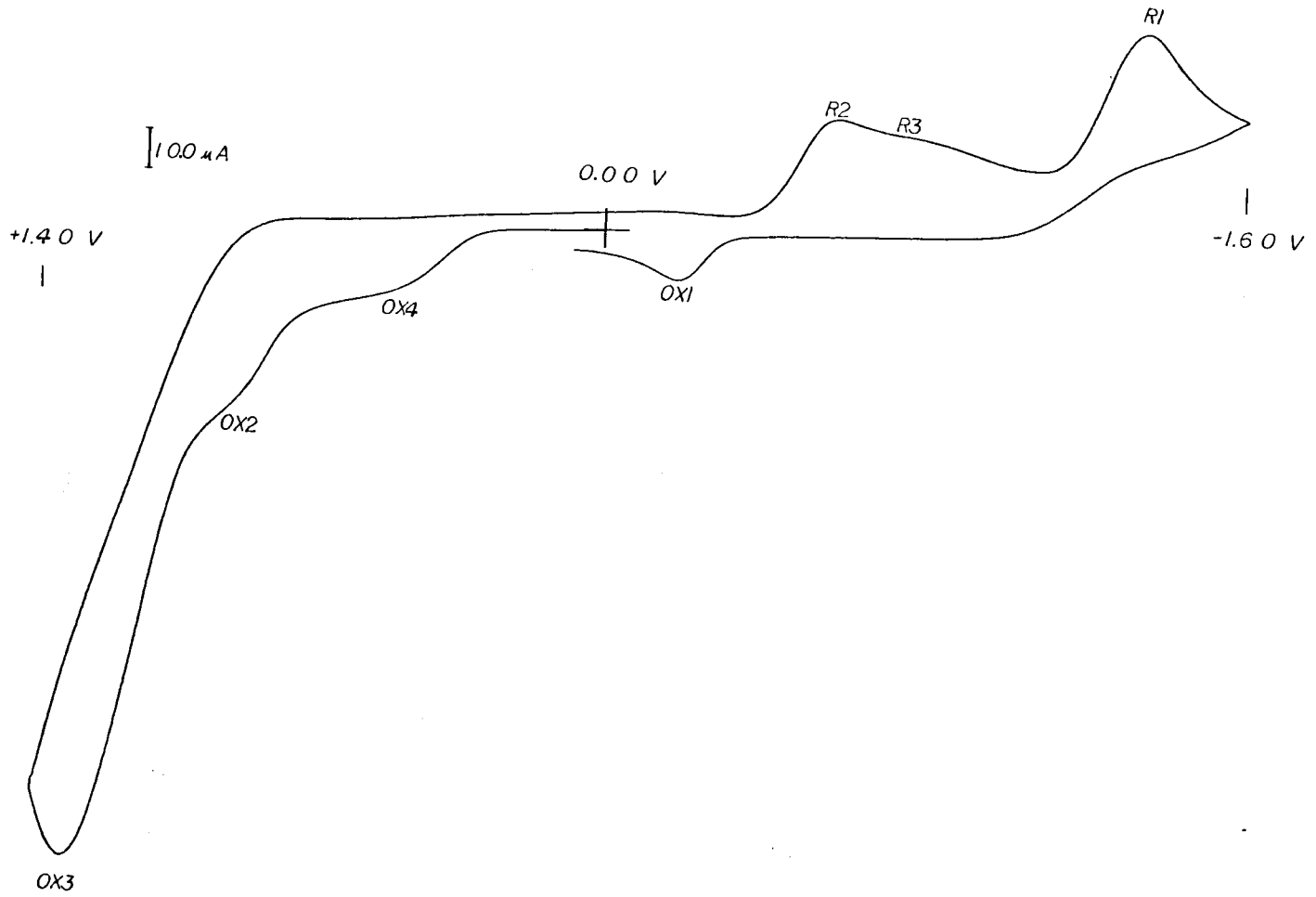


Figure 8. Cyclic voltammogram of 1 with excess CO and excess TBACl.

Conditions: Conc. 5.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

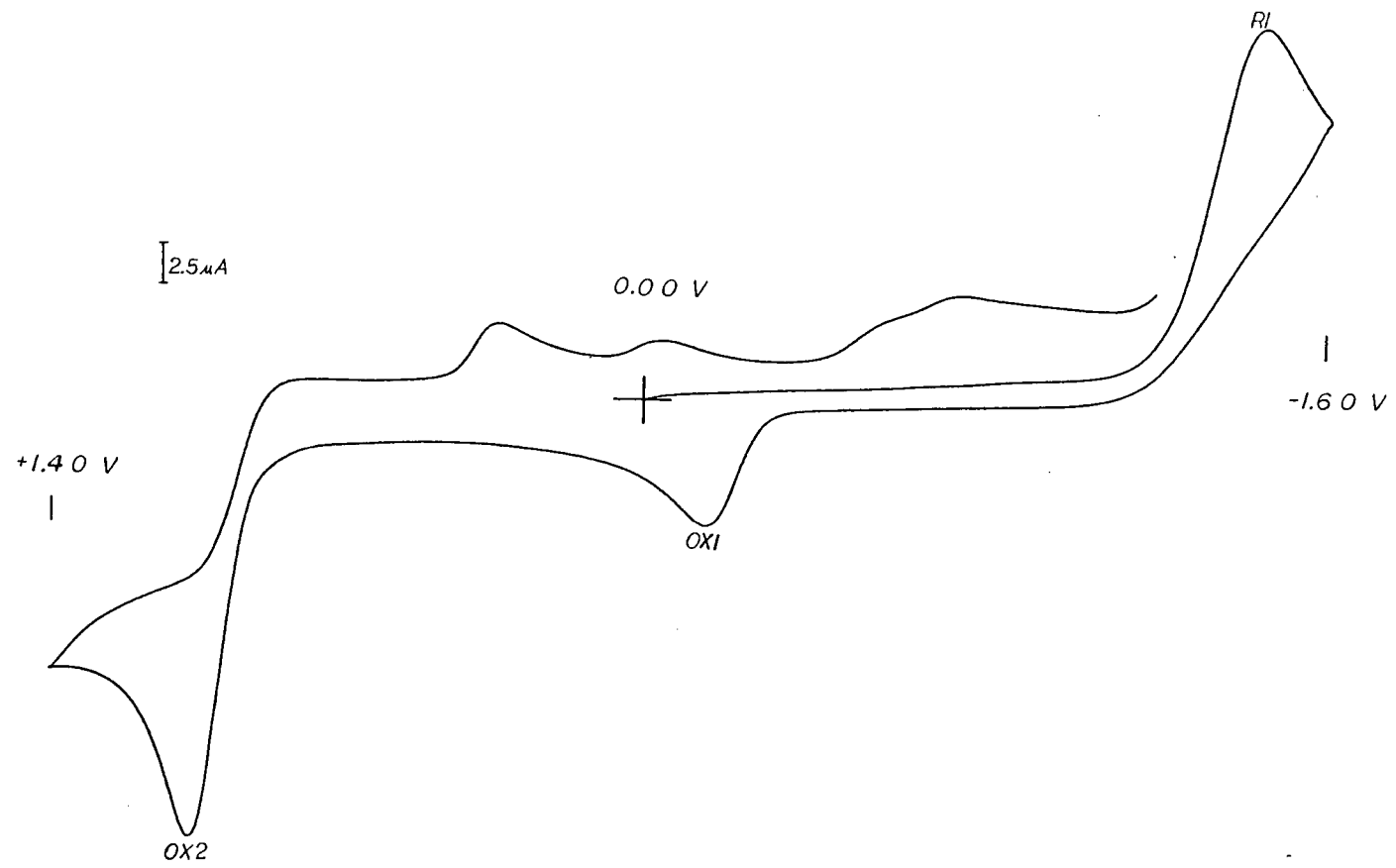


Figure 9. Cyclic voltammogram of 24 with excess CO.

Conditions: Conc. 3.0×10^{-4} M1 0.10 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

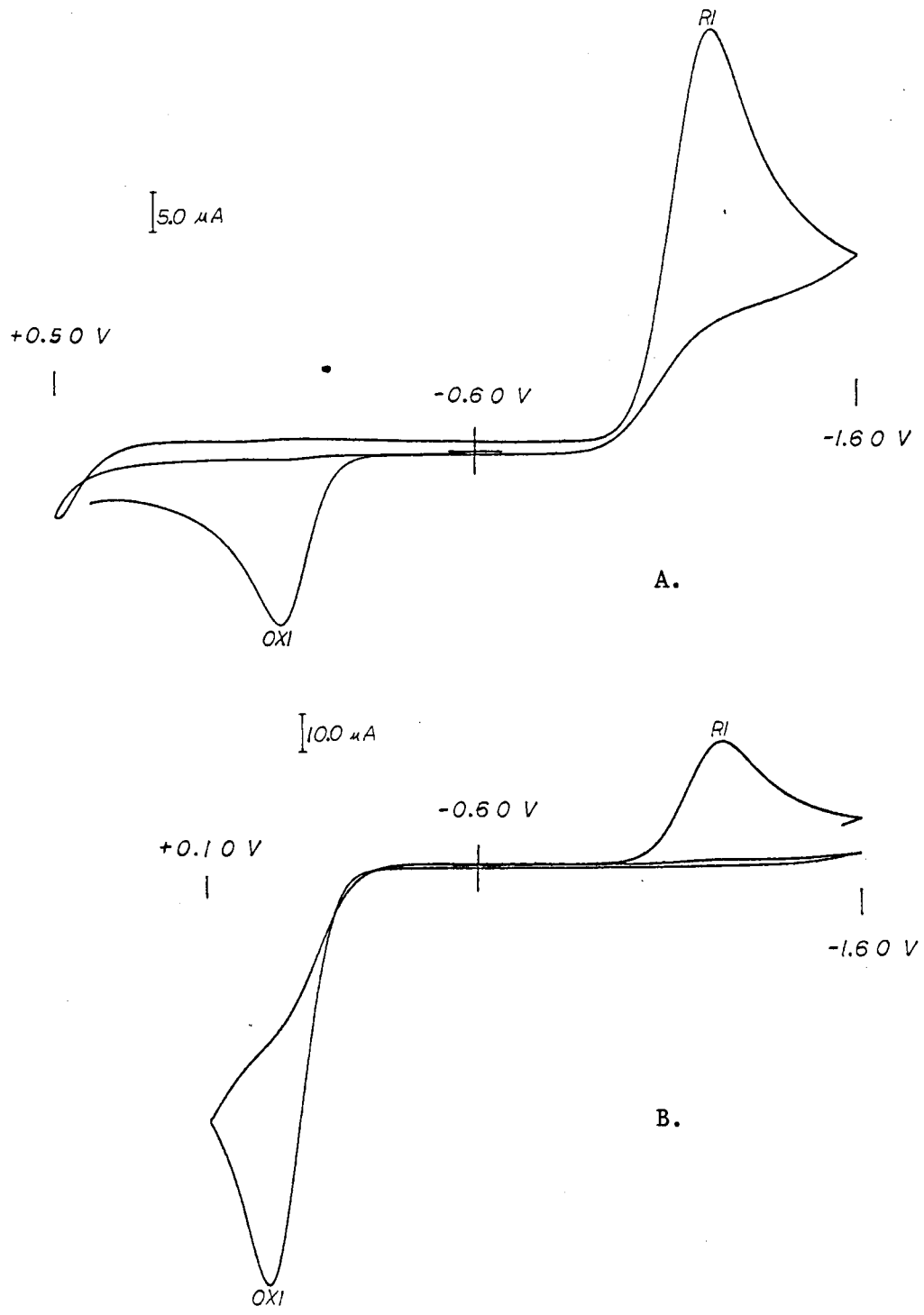


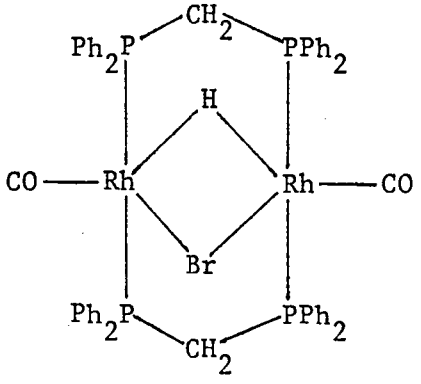
Figure 10. Cyclic voltammogram of 1 with excess CO before (A) and after (B) reduction at -1.45 volts.

Conditions A: $Conc_1$ 4.0×10^{-4} M; 0.10 M TBABr/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

Conditions B: $Conc_1$ 9.1×10^{-4} M; 0.15 M TBABr/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

the coulombs passed during the electrolysis shows R1 in Figure 7 (p 37) to represent an apparent two-electron process.

The solution containing the reduced complex was stripped of CH_2Cl_2 and stirred in water for two hours to achieve separation of the rhodium complex from the TBABr. A voltammogram of the isolated complex was not similar to the voltammogram (Figure 10B, p 41) of the reduced complex prior to separation. This would imply that the complex had been altered during the separation procedure. The IR spectrum of the isolated dimer shows ν_{CO} at 1958 cm^{-1}(s) and 1937 cm^{-1}(sh-m) indicating the presence of two terminal carbonyls. Since CO frequencies for Rh(0) dimers were expected to occur at lower frequencies than those observed, it was concluded that the isolated complex may no longer be a Rh(0) dimer. The ν_{CO} for the isolated complex appeared to be much closer to the ν_{CO} obtained for the Rh(I) hydride complex 22 (p 15)(1962 cm^{-1} and 1945 cm^{-1})[13] produced by the addition of H^+ to the Rh(0) complex 20 (p 15). It is therefore postulated that a highly reactive Rh(0) dimer was generated during the reduction which then accepted H^+ from water in the work-up. If this process did occur then the isolated complex is probably similar to the hydride complex 22 (p 15). The Rh(I) dimer would need to acquire an anion from the electrolysis solution in the form of either a counter ion or a coordinated ligand. The isolated complex was found to be soluble in ether which would imply a nonpolar, neutral rhodium dimer thus suggesting the anion would be a coordinated ligand. The elemental analysis shows the presence of bromine which would strengthen the hypothesis that a Rh(I) dimer was isolated. To maintain symmetry and an electron count of 18 the Br^- is considered to be a bridging ligand thus for the isolated complex, 30 (p 28) is considered to be the most acceptable structure.



30

The elemental analysis is consistent with the proposed formula of 30 (p 28) if three water molecules are assumed to be present. Until ^{1}H NMR can be performed on 30 (p 28) the presence of a hydride is only conjecture.

The electrochemistry of 2 (p 5) in the CH_2Cl_2 and TBAH system as was expected is vastly different from the electrochemistry of 1 (p 5). The voltammogram of 2 (p 5)(Figure 11, p 44) in this system shows a large reduction wave (R4) near -1.52 volts which does not have a corresponding oxidation wave. The small reduction waves (R2 and R3) have been shown to be associated with the oxidation wave (Ox1) which occurs at +0.44 volts. Exhaustive coulometry suggests that this oxidation process involves the removal of one electron per dimer. However, attempts to isolate a $Rh(I\frac{1}{2})$ dimer were unsuccessful. The strong oxidation wave (Ox2) at -1.37 volts is coupled with a weak reduction wave (R1) at -0.10 volts.

The effect of excess Cl^- on 2 (p 5) was then examined so a comparison with 1 (p 5) could be made. Figure 12 (p 45) at first glance appears to be only slightly different from Figure 11 (p 44). When exhaustive coulometry is performed at +0.65 volts, an apparent electron count of two is obtained. Since an electron count of one is obtained in the absence of excess Cl^-,

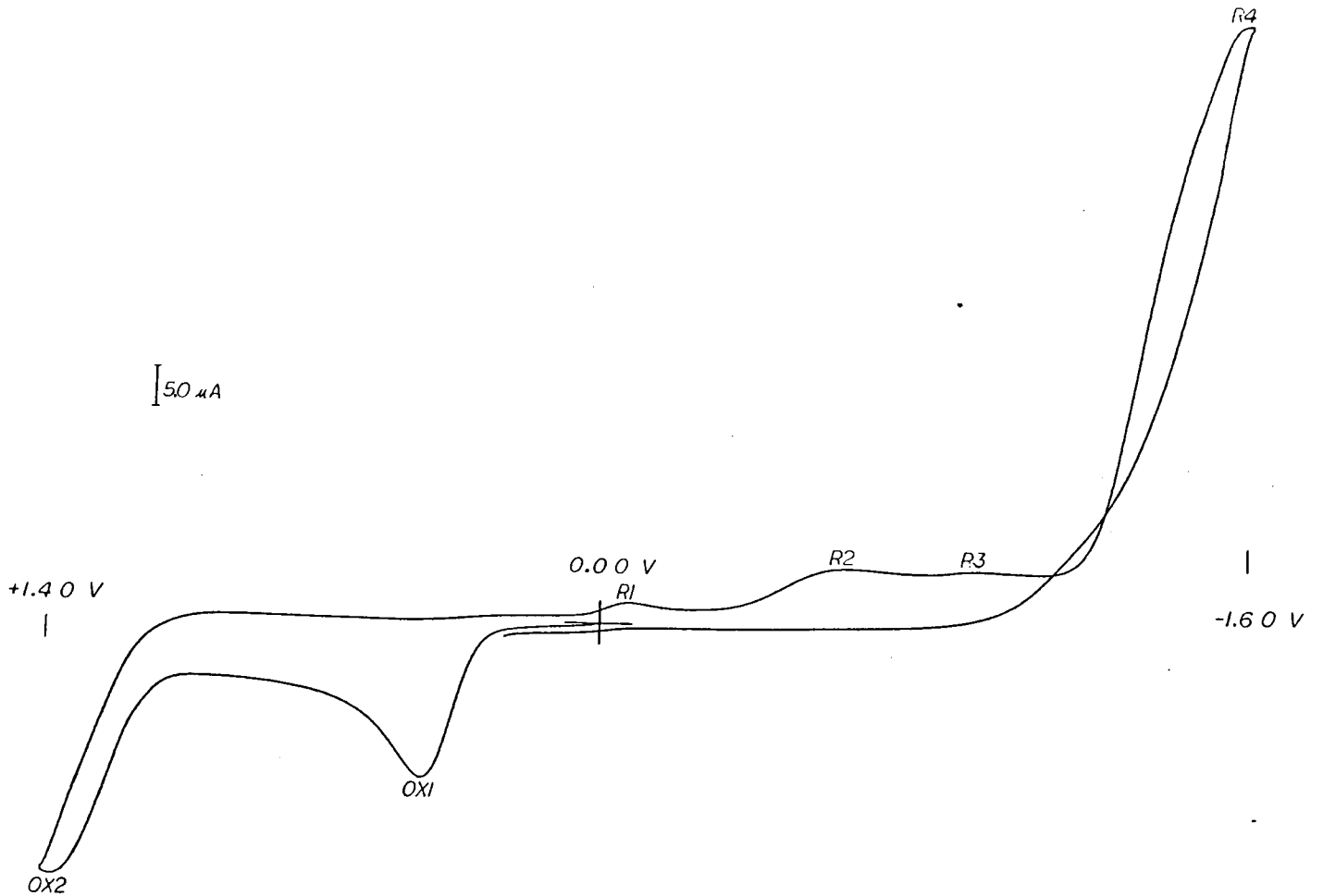


Figure 11. Cyclic voltammogram of 2.

Conditions: Conc. 4.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

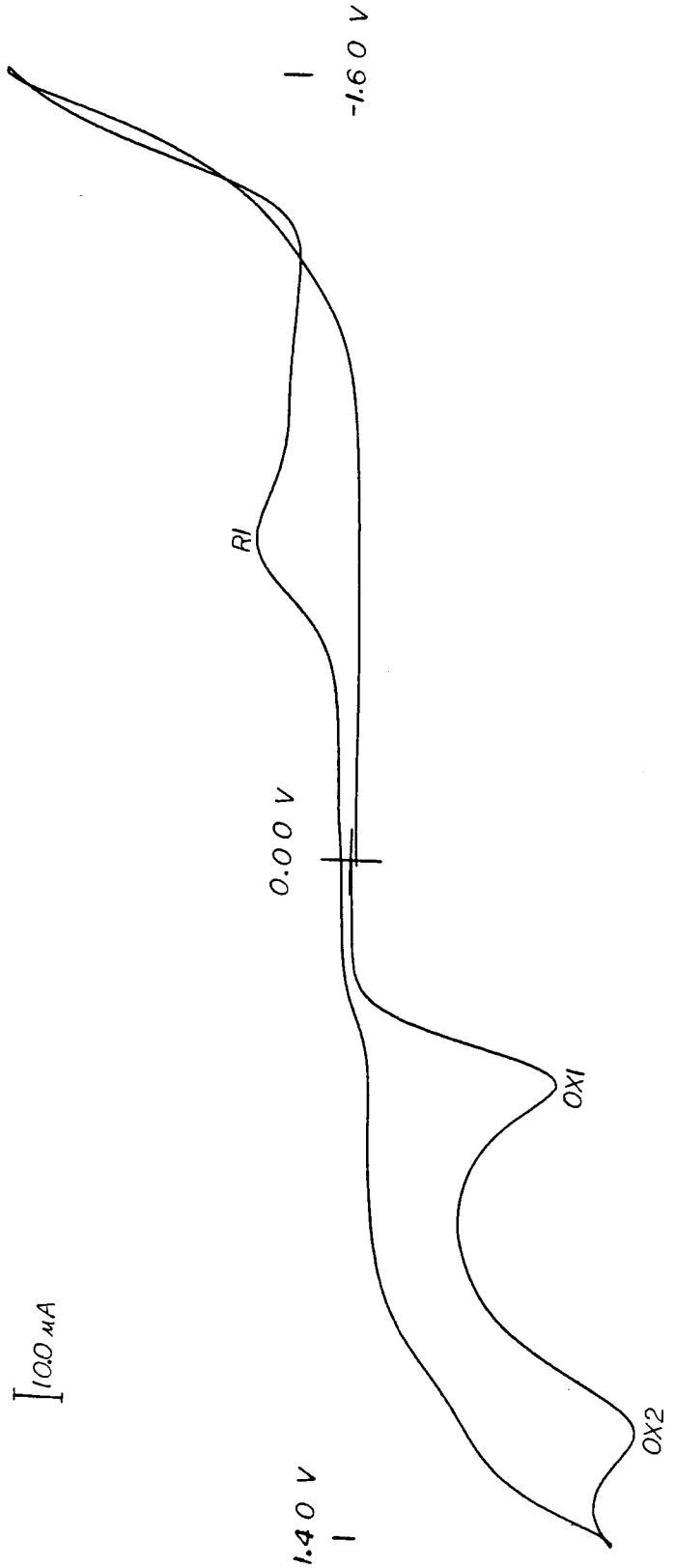


Figure 12. Cyclic voltammogram of 2 with excess TBACl.

Conditions: Conc. 4.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

the free excess Cl^- is obviously affecting the electrochemical behavior of 2 (p 5). If the oxidation wave (Ox2) at +1.16 volts is due to the oxidation of the excess Cl^-, the oxidation wave corresponding to Ox2 of Figure 11 (p 44) has either disappeared or moved beyond the solvent limits due to the addition of excess Cl^-.

It appears that in the presence of excess Cl^-, 2 (p 5) is behaving like 1 (p 5). This suggests that a Rh(II) dimer could possibly be isolated from the oxidized solution. The voltammogram (Figure 13, p 47) of the oxidized solution shows that the oxidation product of 2 (p 5) is unlike 27 (p 25). The fact that the product can be reduced back to the original complex signifies that CO is not lost during the electrolysis. The IR spectrum of the residue which remains when CH_2Cl_2 is removed and the IR spectrum of the isolated rhodium product show ν_{CO} at 1992 cm^{-1} (sh-m) and 1982 cm^{-1} (s). These frequencies suggest the presence of at least two terminal carbonyls. Even though the elemental analysis shows the chlorine to be slightly higher than calculated, the complex has been formulated as $[Rh_2(CO)_2Cl_3(dam)_2][PF_6]$ (28, p 26). Once again to maintain the symmetry the structure is considered to contain a bridging Cl^-. There are several reported Rh(II) dimers which have been shown by their magnetic behavior to contain a rhodium-rhodium bond.[11,19] These reported dimers were all found to be diamagnetic, which would indicate a preference for an even electron count on each rhodium since Rh(II) is a d^7 ion. If by analogy to other Rh(II) dimers, complex 28 (p 26) is diamagnetic (magnetic measurements have not been made), an 18 electron count for each rhodium means the adoption of a rhodium-rhodium bond. Three different isomers are possible (28a, 28b, 28c) and at this time no data have been collected which would indicate which isomer(s) has been isolated.

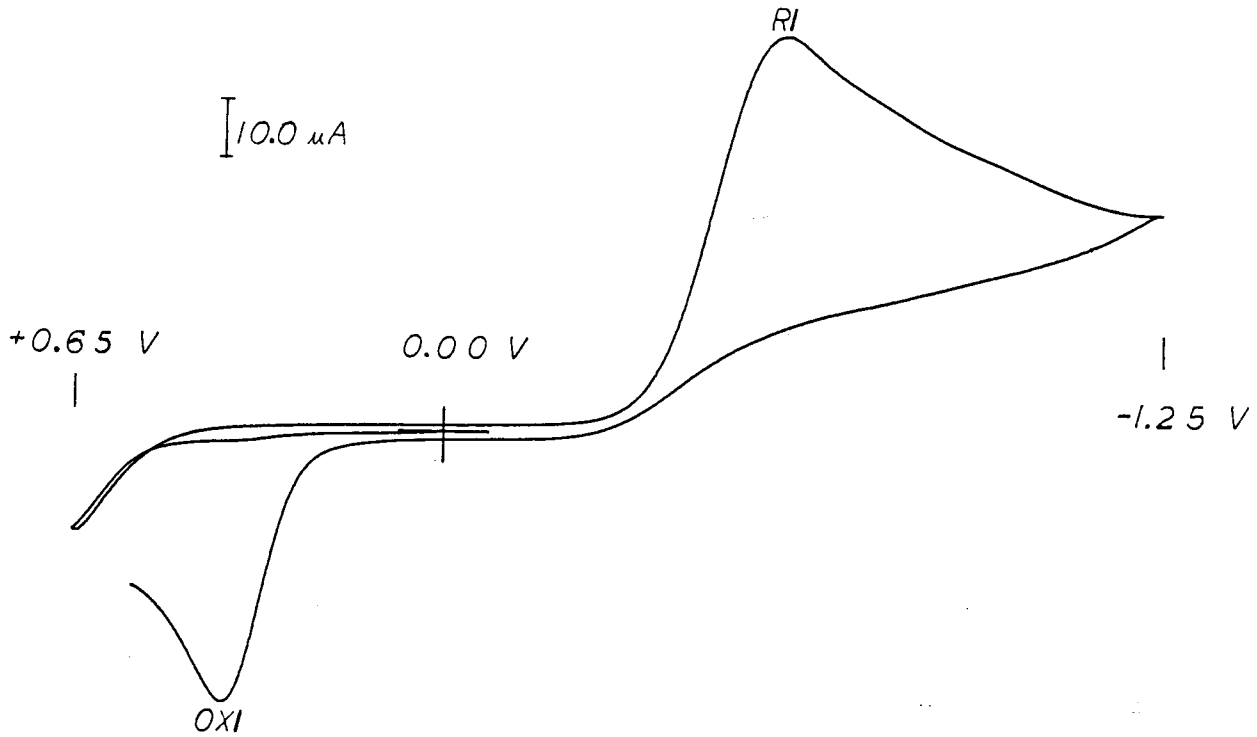
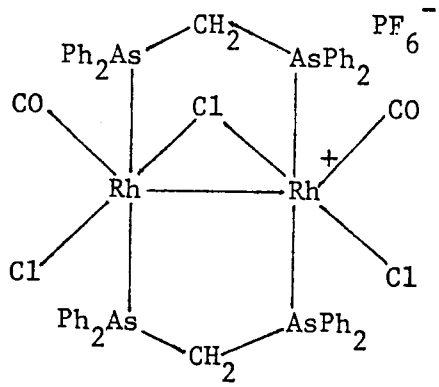
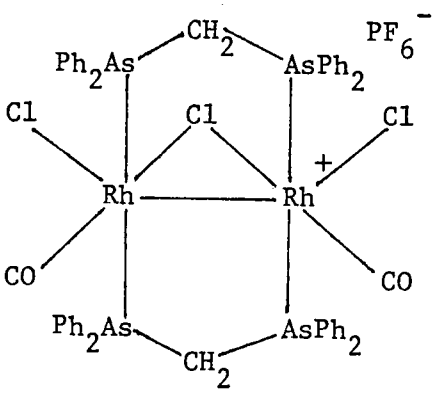


Figure 13. Cyclic voltammogram of 2 with excess TBACl after oxidation at +0.65 volts.

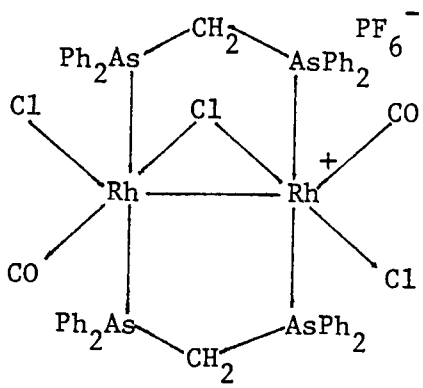
Conditions: Conc. 1.0×10^{-3} M; 0.15 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.



28a



28b



28c

Since $[Rh_2(CO)_3Cl(dam)][Cl]$ cannot be isolated there was no reason to expect that, in the presence of excess CO, 2 (p 5) would behave like 1 (p 5). The existence of an equilibrium between 2 (p 5) and a CO-substituted complex in solution has been suggested and for this reason it was felt that the cyclic voltammetry of 2 (p 5) in the presence of CO might exhibit a very complicated voltammogram. The voltammogram (Figure 14, p 49), however, appears to be even simpler than the voltammogram of 4 (p 6)(Figure 7, p 37). The reduction (R2) at -1.18 volts, however, did not have a corresponding oxidation wave but there was a free Cl^- wave (Ox2) at +1.11

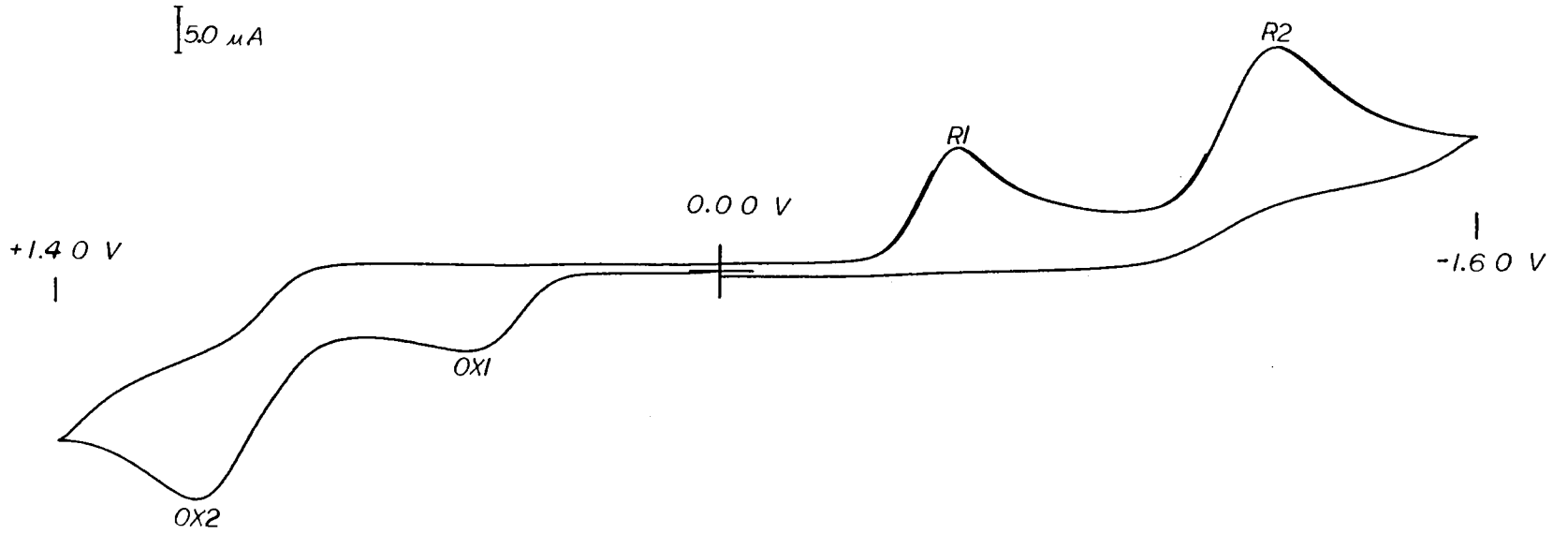


Figure 14. Cyclic voltammogram of 2 with excess CO.

Conditions: Conc. 4.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

volts. The free Cl^- would suggest that at least some of 2 (p 5) upon bubbling with CO was being converted to a complex analogous to 4 (p 6). The remaining waves were an oxidation wave (Ox1) at +0.56 volts and its corresponding reduction wave (R1) at -0.51 volts.

Efforts to obtain an electron count for R2 (Figure 14, p 49) and to produce an isolable product were futile. During exhaustive coulometry at -1.40 volts the solution turned from an initial dark red-orange to a bright orange at two electrons but the cathodic current never decreased to the background level. The electrolysis was eventually stopped after the electron count was over three. No further attempts to characterize R2 were made.

Since 7 (p 9) has a structure similar to 1 (p 5) and 2 (p 5), it was of interest to ascertain whether electrochemical oxidation of 7 (p 9) in the presence of Br^- would produce a product similar to 19a (p 15), 27 (p 25), or 28 (p 26).

The voltammogram (Figure 15A, p 51) of complex 7 (p 9) in CH_2Cl_2, TBAH and a 10 fold molar excess of Br^- as TBABr, shows a strong oxidation wave (Ox1) at +0.38 volts which, as shown in Figure 15B (p 51) is associated with two reduction waves (R1 and R2) at -0.46 volts and -0.68 volts respectively. Exhaustive coulometry at +0.60 volts on a solution of 7 (p 9) containing a 25 fold molar excess of Br^- shows the oxidation (Ox1) to be a two electron process. The voltammogram (Figure 16, p 52) of the oxidized solution shows a broad reduction wave (R1) at -0.63 volts. The Rh(II) dimer was isolated with methanol by the same process used to isolate the oxidation products of 1 (p 5) and 2 (p 5) in the presence of excess Cl^-. The isolated complex gives IR and UV-Visible spectra which are essentially identical to those reported for complex 19a (p 15). The elemental analysis

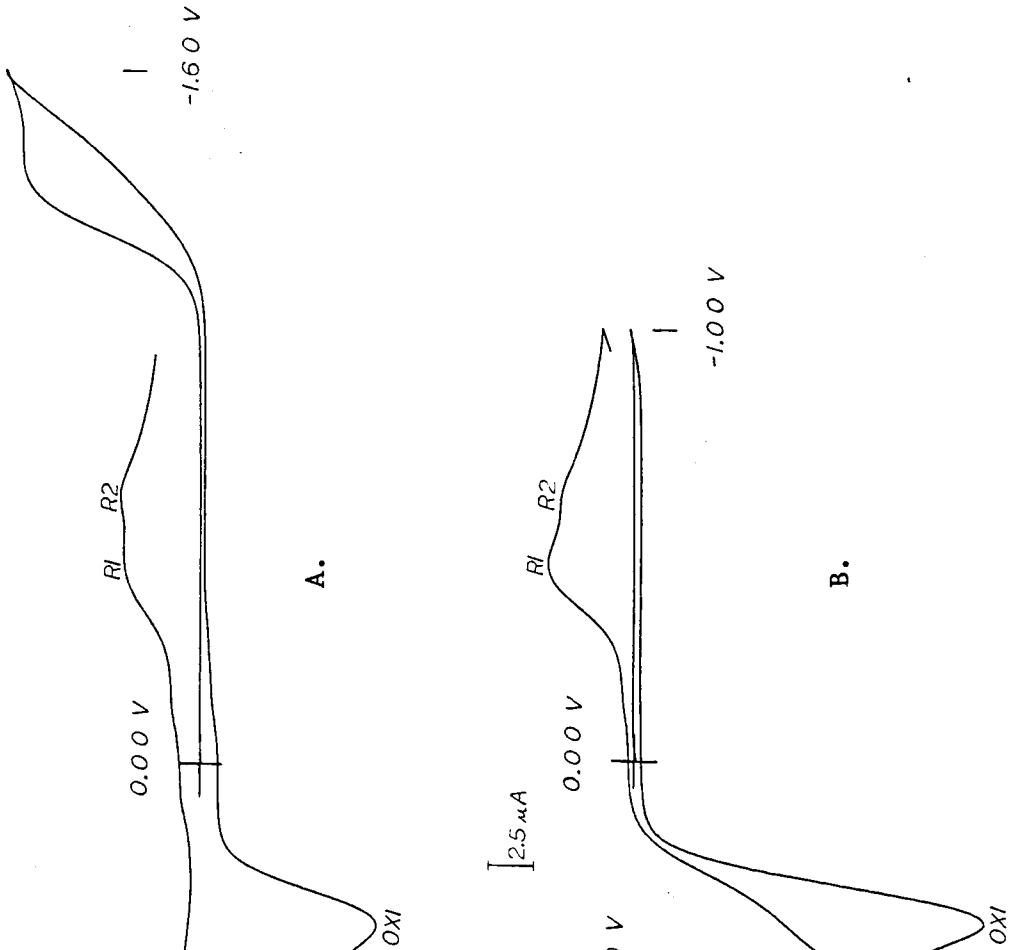


Figure 15. Cyclic voltammogram of 7 with excess TBABr.

Conditions A and B: Conc. 4.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

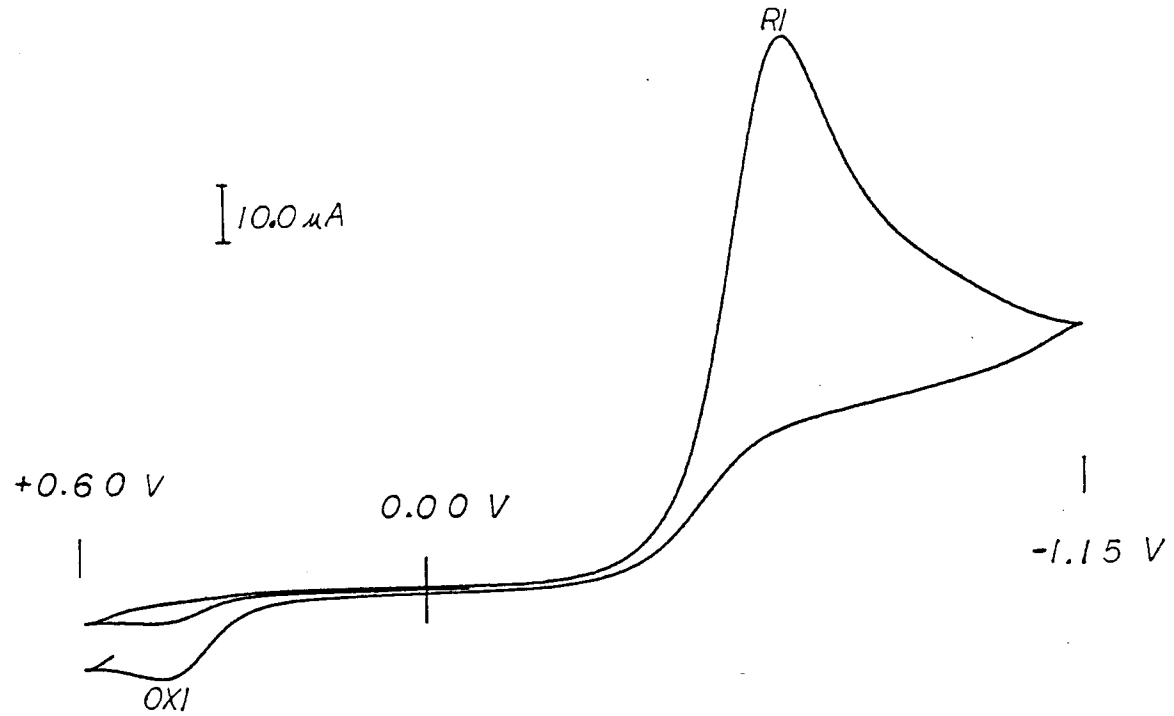


Figure 16. Cyclic voltammogram of 7 with excess TBABr after oxidation at +0.60 volts.

Conditions: Conc. 2.5×10^{-4} M; 0.15 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

is also consistent with 19a (p 15) even though the bromine percentage is slightly higher than calculated.

The last complex of interest in this work is complex 29 (p 27), which is the PF_6^- analog of 15 (p 13). Complex 29 (p 27) is similar to 24 (p 23) but with the two terminal CO ligands having been replaced by the ligand $(CH_3)_3CNC$. The voltammetry of 29 (p 27) in CH_2Cl_2 and TBAH leads to an extremely complicated voltammogram (Figure 17, p 54). The presence of three very close quasi-reversible couples made the voltammogram impossible to analyze. After an apparent electron count of one, exhaustive coulometry at +1.03 volts produced the voltammogram in Figure 18 (p 55). Many attempts were made, however, to get electron counts for various couples but these efforts were unsuccessful.

The success achieved with exhaustive oxidation of 1 (p 5), 2 (p 5) and 7 (p 9) in the presence of excess halide warranted a similar investigation with complex 26 (p 25). Figure 19A (p 56) is a voltammogram of 26 (p 25) in the presence of a 10-molar excess of Cl^-. The oxidation wave (Ox1) at +0.44 volts as shown in Figure 19B (p 56) is associated with three reduction waves (R1, R2 and R3) which occur at -0.26 volts, -0.47 volts and -1.10 volts respectively. Exhaustive coulometry at +0.60 volts shows Ox1 to represent an apparent two-electron process. The voltammogram (Figure 20, p 57) of the oxidized solution still exhibits the three reduction waves (R1, R2 and R3) but the reduction wave (R2) at -0.52 volts represents the predominant oxidation product.

The Rh(II) dimer was isolated with methanol as previously discussed. The IR spectrum does not exhibit peaks which can be assigned to ν_{CO} but does show ν_{RNC} at 2176 cm^{-1} (s) and 2225 cm^{-1} (w) and PF_6^- peaks at 839 cm^{-1} (s) and 558 cm^{-1} (m). This spectrum indicates the presence of at least two

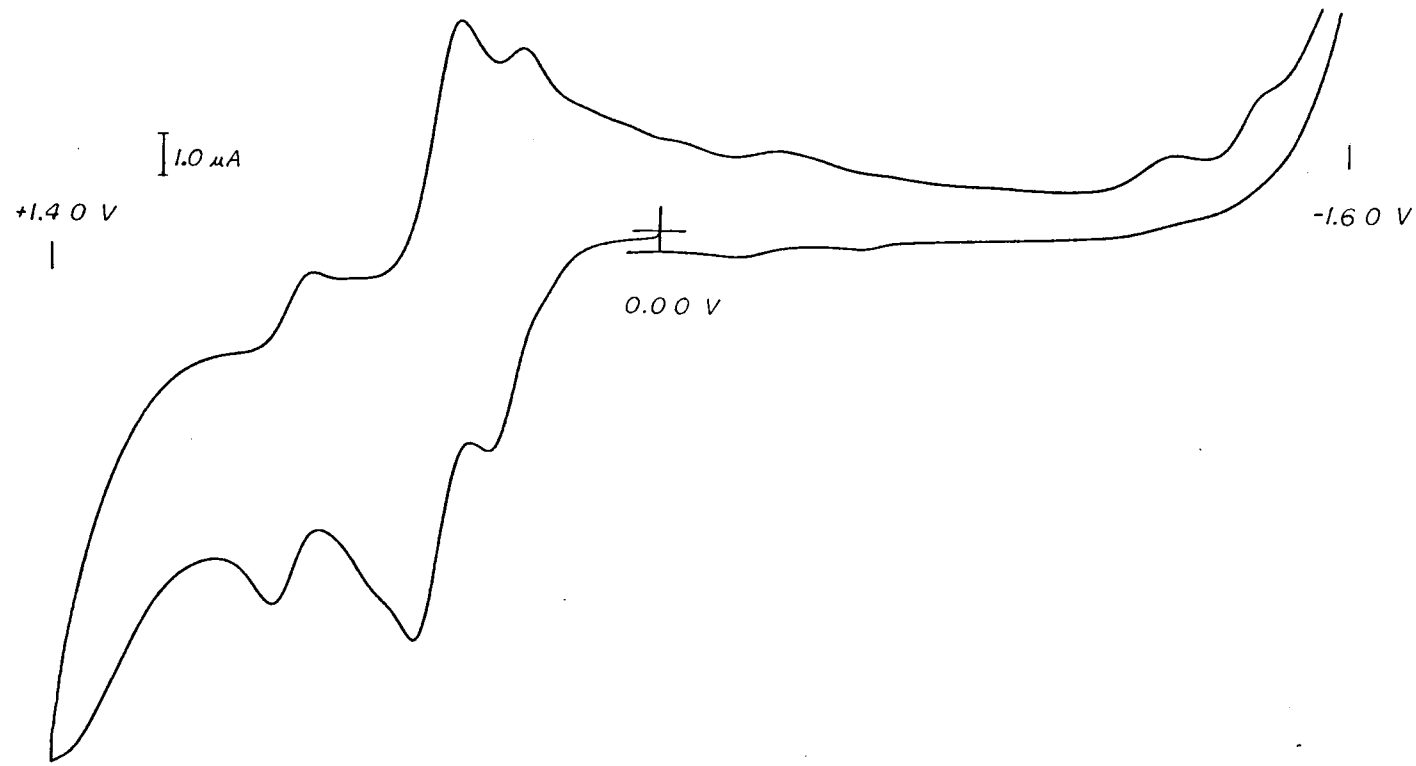


Figure 17. Cyclic voltammogram of 26.

Conditions: Conc. 5.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 50 mV sec^{-1}; SCE.

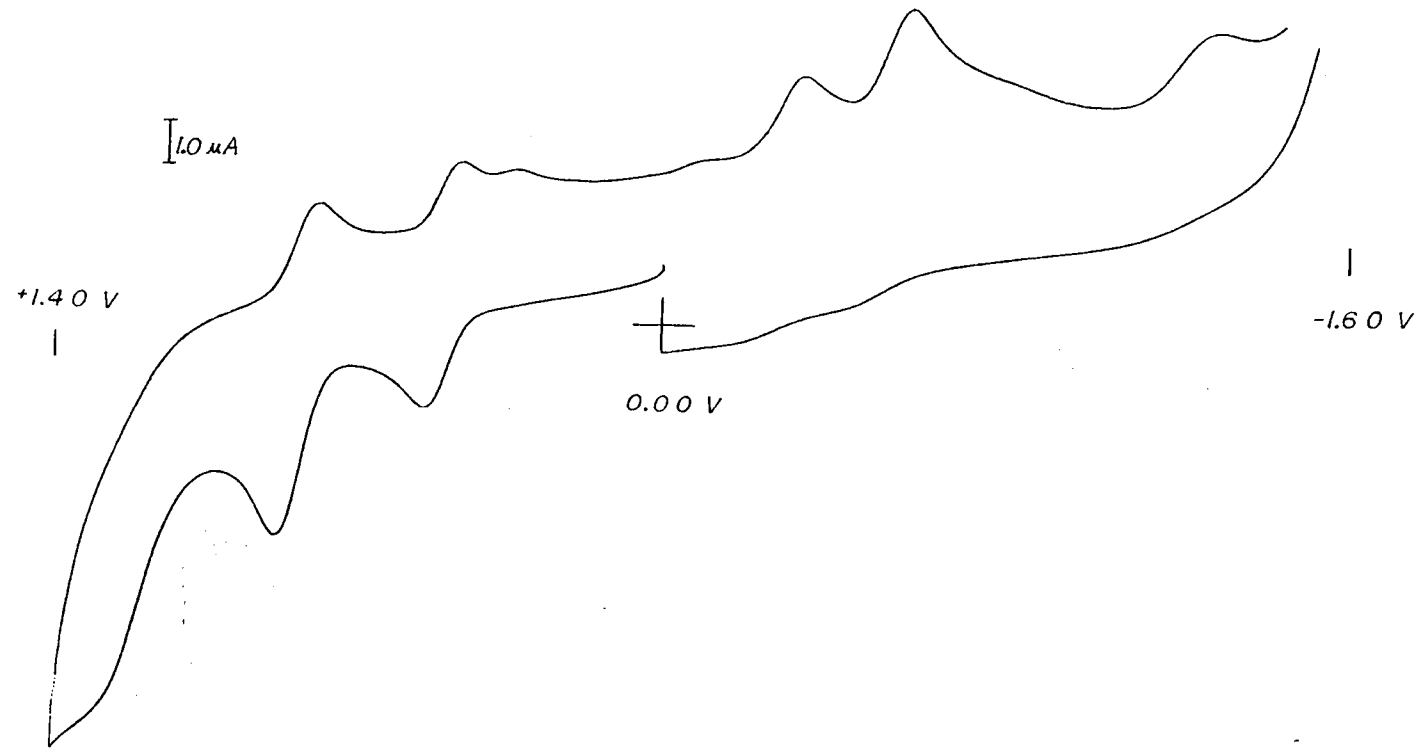


Figure 18. Cyclic voltammogram of 26 after oxidation at +1.03 volts.

Conditions: Conc. 3.5×10^{-4} M; 0.20 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

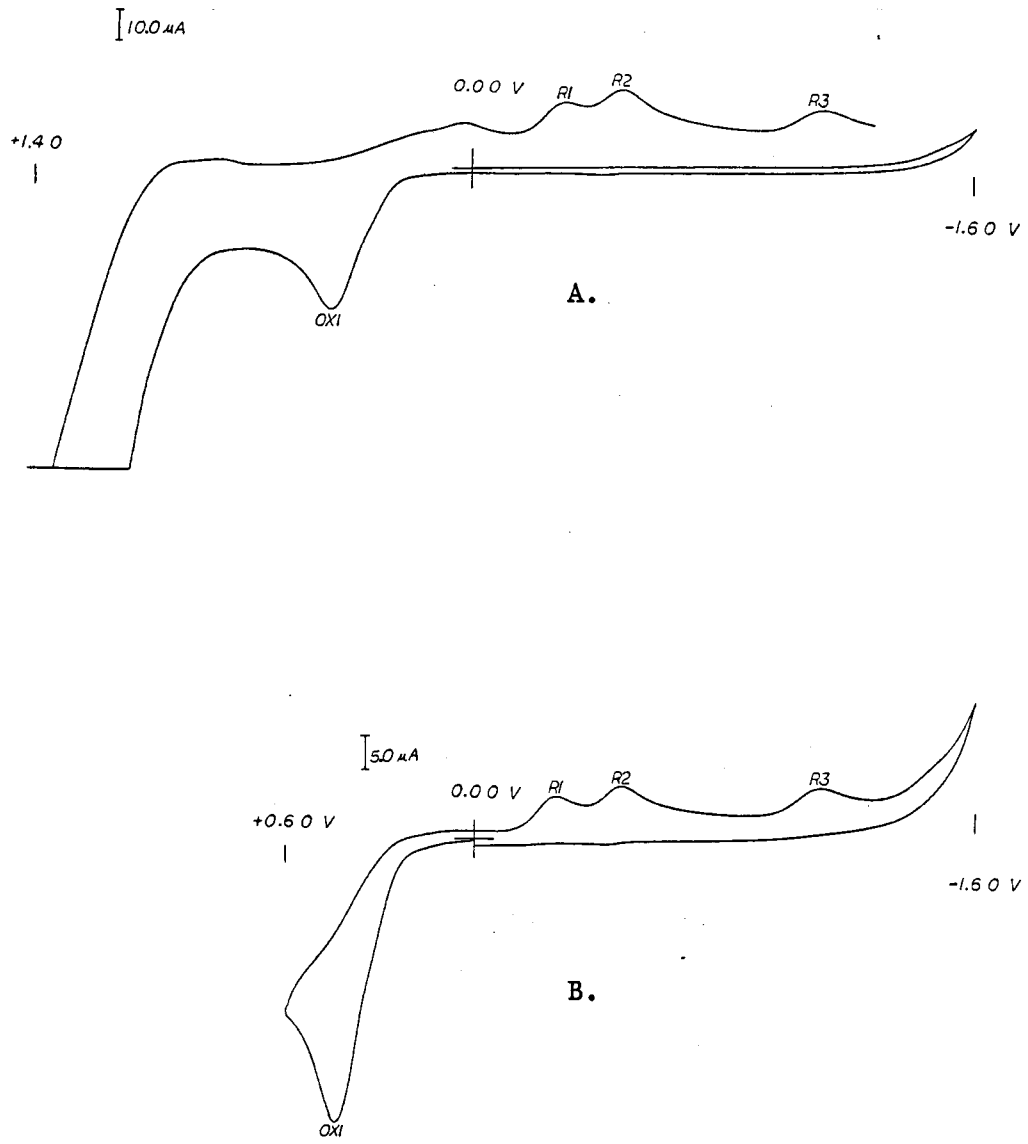


Figure 19. Cyclic voltammogram of 26 with excess TBACl.

Conditions A and B: Conc. 5.0×10^{-4} M; 0.10 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

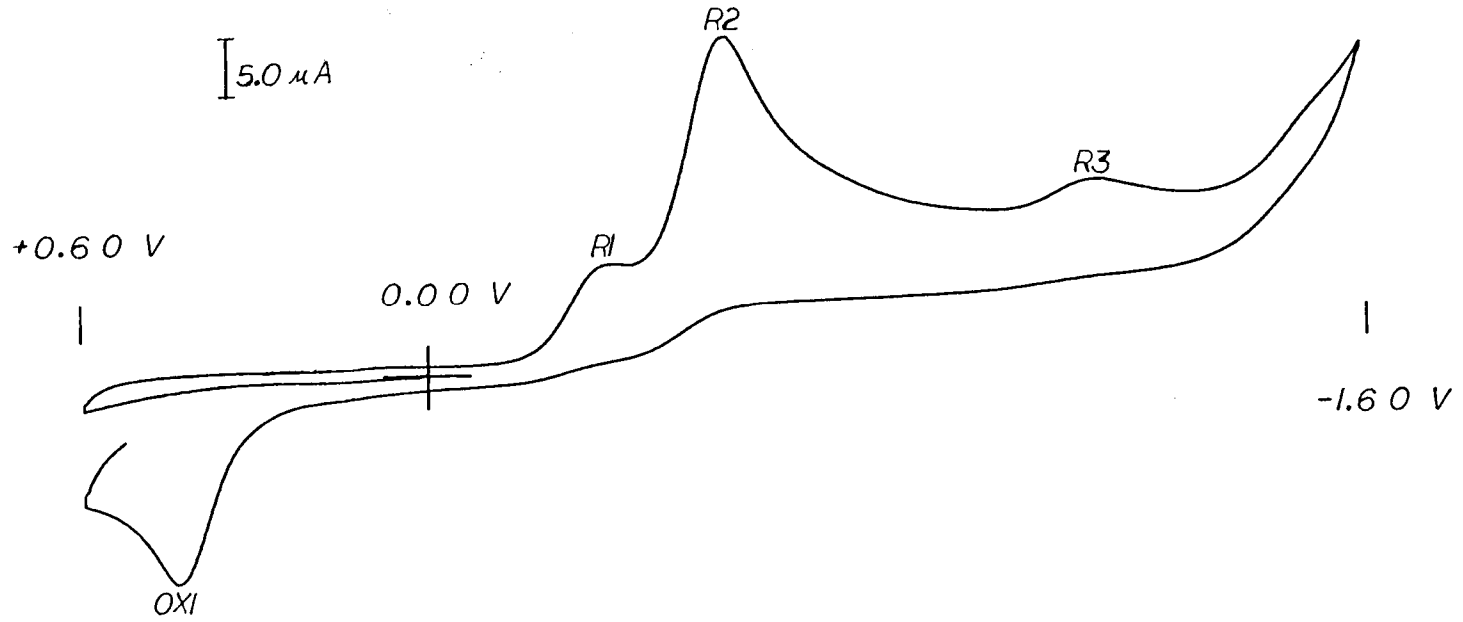
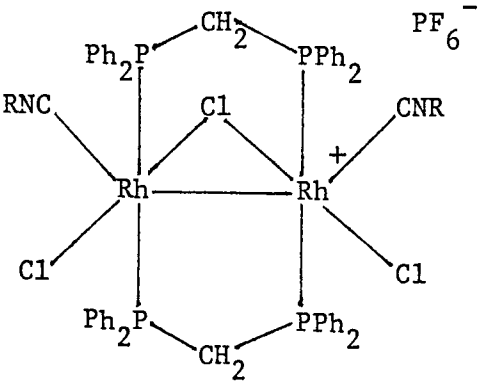


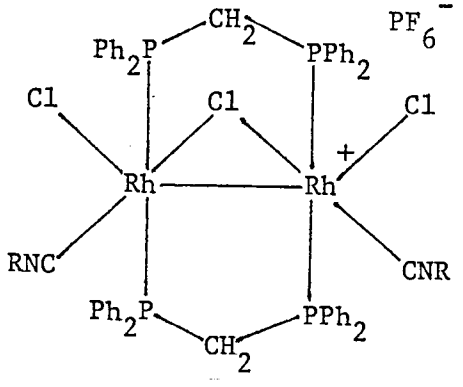
Figure 20. Cyclic voltammogram of 26 with excess TBACl after oxidation at +0.60 volts.

Conditions: Conc. 5.0×10^{-4} M; 0.20 M TBAH/CH_2Cl_2; sweep rate 100 mV sec^{-1}; SCE.

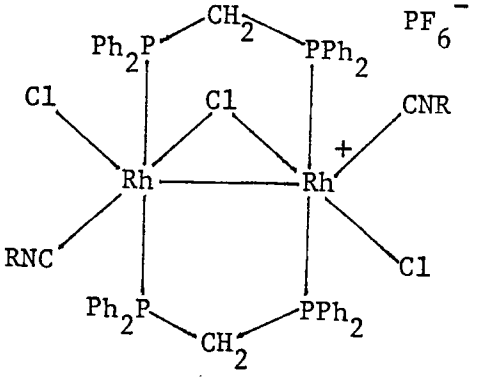
terminal RNC ligands in the complex. The elemental analysis agrees with the formula $[Rh_2Cl_3(t\text{-}C_4H_9NC)_2(dpm)_2][PF_6]$. In order to formulate a symmetrical species and obtain a 16 electron count for each rhodium, a bridging Cl^- has been assumed in order to give complex 29 (p 27). As with 28 (p 26) three isomers are possible (29a, 29b and 29c) and sufficient data have not been collected which would indicate which isomer(s) has been isolated.



29a



29b



29c

The dpm and analogous dam rhodium dimers examined in this work exhibit vast differences in their electrochemical behaviors. The electrochemistry of these complexes provides no additional insight into why

their chemical behaviors are so different. It has been shown, however, that with the aid of electrolysis new rhodium complexes can be isolated which possibly cannot be prepared by chemical processes.

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VITA

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