

To the Graduate Council:

I am submitting herewith a dissertation written by Louis Joseph Tortorelli entitled "Synthesis, Structure, Chemical and Electrochemical Investigation of Some Dinuclear Rhodium Complexes." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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SYNTHESIS, STRUCTURE, CHEMICAL AND
ELECTROCHEMICAL INVESTIGATION OF SOME
DINUCLEAR RHODIUM COMPLEXES

A Dissertation
Presented for the
Doctor of Philosophy
Degree
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Louis Joseph Tortorelli

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DEDICATED TO MY MOM AND DAD

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ABSTRACT

The electrochemical oxidation of trans-Rh₂(μ-dppm)(CO)₂Cl₂ (dppm = Bis(diphenylphosphino)methane) in the presence of chloride has been investigated. The oxidation affords an unsymmetrical dirhodium(II) complex, Rh₂Cl₃(μ-Cl)(CO), 14, which is readily converted to a symmetrical complex, [Rh₂(μ-dppm)₂Cl₂(μ-CO)(μ-Cl)](PF₆), 4. Complex 4 has been shown to undergo addition reactions with chloride, carbon monoxide and t-butylisocyanide to generate other new dirhodium(II) complexes.

The electrochemical and chemical reactivity of Rh₂(μ-dppp)₂-Cl₂(μ-CO), 5, (dppp = diphenylphosphinopyridine) have been examined. Electrochemical oxidation of 5 in CH₂Cl₂/TBAH/Cl⁻ affords Rh₂(μ-dppp)₂Cl₃(μ-Cl)CO, 9; while in CH₂Cl₂/TBAN/Cl⁻, Rh₂(μ-dppp)₂Cl₃(μ-NO₃), 7, is generated. The crystal structure of 7 has been obtained which displays a disorder involving the CO on one rhodium atom, and the staggered Cl on the second rhodium atom. Complex 9 has been shown to undergo addition reactions with carbon monoxide and t-butylisocyanide to afford other dirhodium(II) complexes.

Novel trans-dppm dinuclear Rh(I) A-frame complexes that contain triazolate, pyrazolate and substituted pyrazolate ligands at the bridgehead position have been studied. Electrochemical investigation of these complexes in CH₂Cl₂ reveals two consecutive one-electron oxidation waves. Paramagnetic species are generated via bulk oxidation between the two waves. ESR spectroscopy has been employed to investigate the nature of these paramagnetic complexes, some of which display a thermochromic effect. Electrochemical

oxidation of some of the diisocyanide complexes has shown that they undergo oxidative-addition reactions. The electrolysis of $[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-Pz})](\text{PF}_6)$ in TBAH/TBAAc/ CH_2Cl_2 generates $[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)$, 40, whose structure has been determined by x-ray structural analysis. The structure of 40 reveals a unique folding of the methylene groups of the dppm ligands over the open site opposite the bridgehead position. The electrochemical behavior of $[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)$ in the presence of a coordinating solvent and a variety of pyridines is also discussed. Reactivity of these A-frame complexes containing terminal t-butylisocyanide ligands with a variety of acids and halogens have been explored.

Electrochemical behavior of novel tetrarhodium(I) complexes of the type, $([\text{Rh}_2(\mu\text{-dppm})_2\text{L}_2]_2\text{Z})(\text{PF}_6)_2$ ($\text{L} = \text{CO}, \underline{\text{t}}\text{-BuNC}$; $\text{Z} = 3,5,3'5'$ -tetramethylbipyrazolate, $4,4'$ -methylenebis(3,5-dimethylpyrazolate)), has been investigated in CH_2Cl_2 .

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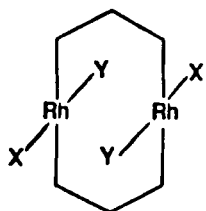
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CHAPTER I

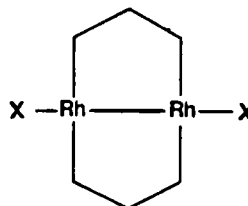
INTRODUCTION

A. Review of Literature

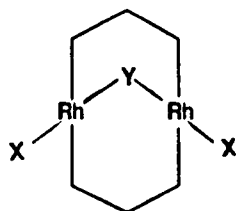
Interest in dinuclear complexes in which two metal atoms are held in proximity to one another is based on their potential versatility as metal catalysts. The metal centers might work synergistically or independently in the activation of various substrates, thus enhancing the reactivity of the dinuclear species over that of the monomer. Bidentate-bridging ligands such as bis(diphenylphosphino)methane (dppm), 2-(diphenylphosphino)pyridine (dppp), (diphenylarsino)(diphenylphosphino)methane (dapm), bis(diphenylarsino)methane (dpam) and other ligands with similar bite sizes not only bind the two metal centers but can also alter dissociation patterns of the metal complexes and promote reactions involving the formation and cleavage of a metal-metal bond. Rhodium dimers containing these ligands as transoid bridging ligands will generally fit into one of four geometrical arrangements: face-to-face, side-by-side, A-frame and double A-frame.



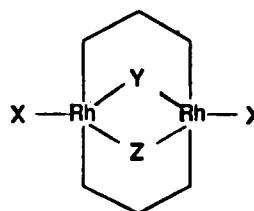
Face-to-Face



Side-by-Side



A-Frame



Double A-Frame

Interaction between metal centers results from the formation of binuclear compounds using dpmm, dapm, dpam, and dppp. As observed in the absorption spectra, this interaction causes a shift to lower energy of the low energy absorption band¹ observed for the monomers - hence the name, proximity shifted absorption band² (Figure 1).

A comparison of the room-temperature absorption spectra,³ and of temperature effects on the emission spectra of rhodium monomers and dimers was undertaken to help determine the fate of this transition in binuclear complexes. For rhodium(I) monomers, the low energy absorption band is generally viewed as a metal-to-ligand transfer ($4d_{z^2} \rightarrow \pi_L$) with some admixture of $5p_z$ character in the π_L -acceptor molecular orbital.³ The low temperature emission spectra and lifetime data are interpreted in terms of a two-level spin-orbit split emitting manifold.^{4,5} The physical assumptions are that: (a) each level is coupled to the ground state by a 1st order process with the radiative and quenching rate constant being temperature independent, and (b) the Boltzman equilibrium is established

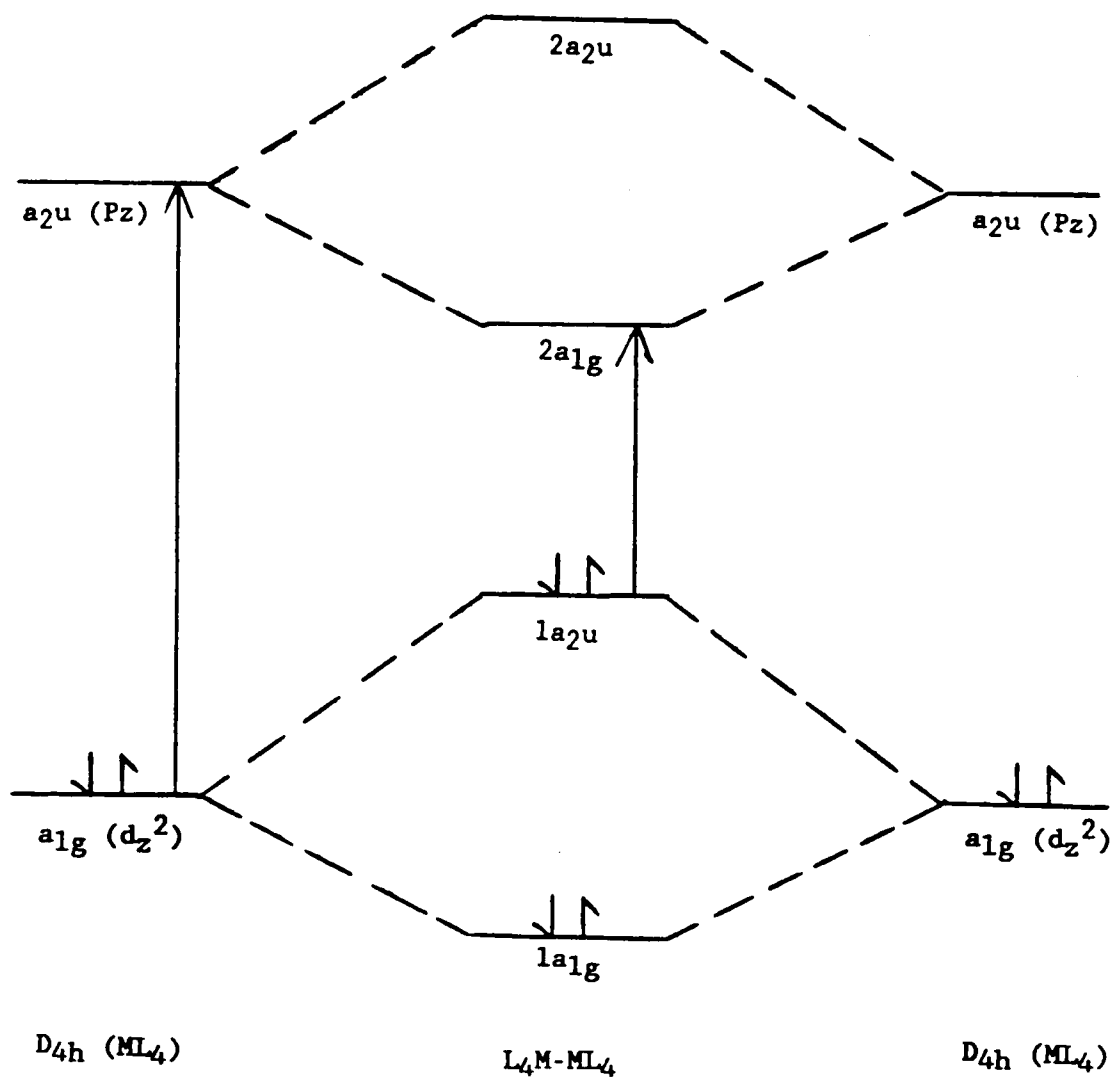


Figure 1. Relative molecular orbital energy diagram showing a comparison of the low energy electronic transition between a monomer (ML_4) and a dimer, constructed from the monomers.

between the levels in lifetimes much shorter than that of the excited manifold.

For the complexes $[\text{Rh}(\text{dppe})_2]\text{ClO}_4$ (dppe = 1,2-bis(diphenylphosphino)ethylene) and $[\text{Rh}(\text{dpae})_2]\text{PF}_6$ (dpae = 1,2-bis(diphenylarsino)ethylene), the energy gap³ ($\Delta\epsilon$) of the two-level emitting manifold is 37.8 and 57.6 cm^{-1} , respectively. The increase in $\Delta\epsilon$ as arsenic is substituted for phosphorus is ascribed to the larger spin-orbit coupling constant of arsenic. This dependence of the energy gap ($\Delta\epsilon$) on the ligand demonstrates the involvement of the ligand through Π orbitals in the low-energy transition.

For dinuclear rhodium complexes, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{n-BuNC})_4](\text{BPh}_4)_2$ (n-BuNC = *n*-butylisocyanide) and $[\text{Rh}_2(\mu\text{-dpam})_2(\text{n-BuNC})_4](\text{BPh}_4)_2$, no significant change in $\Delta\epsilon$ was observed upon changing the bridging ligand from dppm to dpam.⁶ The lack of ligand dependence on $\Delta\epsilon$ for these Rh(I) dimers leads to the conclusion that the low-energy transition is primarily metal-centered.

For face-to-face dimers of the type $[\text{Rh}_2(\mu\text{-dppm})_2(\text{n-BuNC})_4](\text{BPh}_4)_2$ with D_{2h} symmetry, this allowed transition is $4d_{z^2} \rightarrow 5p_z$ or $^1A_g \rightarrow ^1B_{1u}$ ($1b_{1u} \rightarrow 2a_g$).⁶ Although the ground state bond order is formally zero, interaction of the $4d_z$ and $5p_z$ orbitals could produce weak Rh-Rh interaction. In the excited state arising from the $4d_{z^2} \rightarrow 5p_z$ transition, a formal bond order of one exists. This correlates with what has been observed by Balch⁷ for face-to-face dimers. He determined that ligand substitution which results in a closer approach of rhodium atoms results in a decrease in the absorption energy. For complexes of the type,

$[\text{Rh}_2(\mu\text{-dppm})_2(\text{RNC})_4]^{2+}$, a decrease in the absorption energy as the R group is changed is as follows: *t*-butyl (523 nm) $\rightarrow$ cyclohexyl (550 nm) $\rightarrow$ methyl (573 nm).

For A-frame complexes with C_{2v} symmetry, the lowest energy transition is the $4d_{z^2} \rightarrow 5p_z$ or $^1A_1 \rightarrow ^1B_2$ ($1b_2 \rightarrow 2a_1$) excitation.⁸ Coordination of a carbonyl into the bridging position opposite the apex ligand in $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})]^+$ causes a redistribution of the energy levels resulting from the interaction of the carbonyl's σ and π^* orbitals with the A-frame's $1a_1$ and $1b_2$ orbitals (Figure 2).⁹ The carbonyl σ orbital will interact with the a_1 orbital with the resulting combination remaining primarily metal in character. The carbonyl π^* orbital will interact with the b_2 orbital of the A-frame resulting in a stabilization of this combination.

This model fits the observed blue shift of the low energy transition in going from $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})]^+$ to $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-CO})]^+$.

Interest in face-to-face dimers such as $\text{Rh}_2(\mu\text{-L}_2)_2(\text{CO})_2\text{Cl}_2$ ($\text{L}_2 = \text{dppm}, \text{dpam}, (\text{diphenylarsino})(\text{diphenylphosphino})\text{methane} (\text{dapm})$) is due to their ability to form A-frame complexes. The crystal structure of trans- $[\text{Rh}_2(\mu\text{-L}_2)_2(\text{CO})_2\text{Cl}_2]$ ^{10,11} ($\text{L}_2 = \text{dppm}, \text{dpam}$) reveals that the geometry about the rhodium atoms is square planar with a trans arrangement of the bridging and terminal ligands. The dimeric unit composed of these parallel square planes is in an eclipsed conformation. It is of particular interest to note that the square planes are not perpendicular to the Rh-Rh vector but

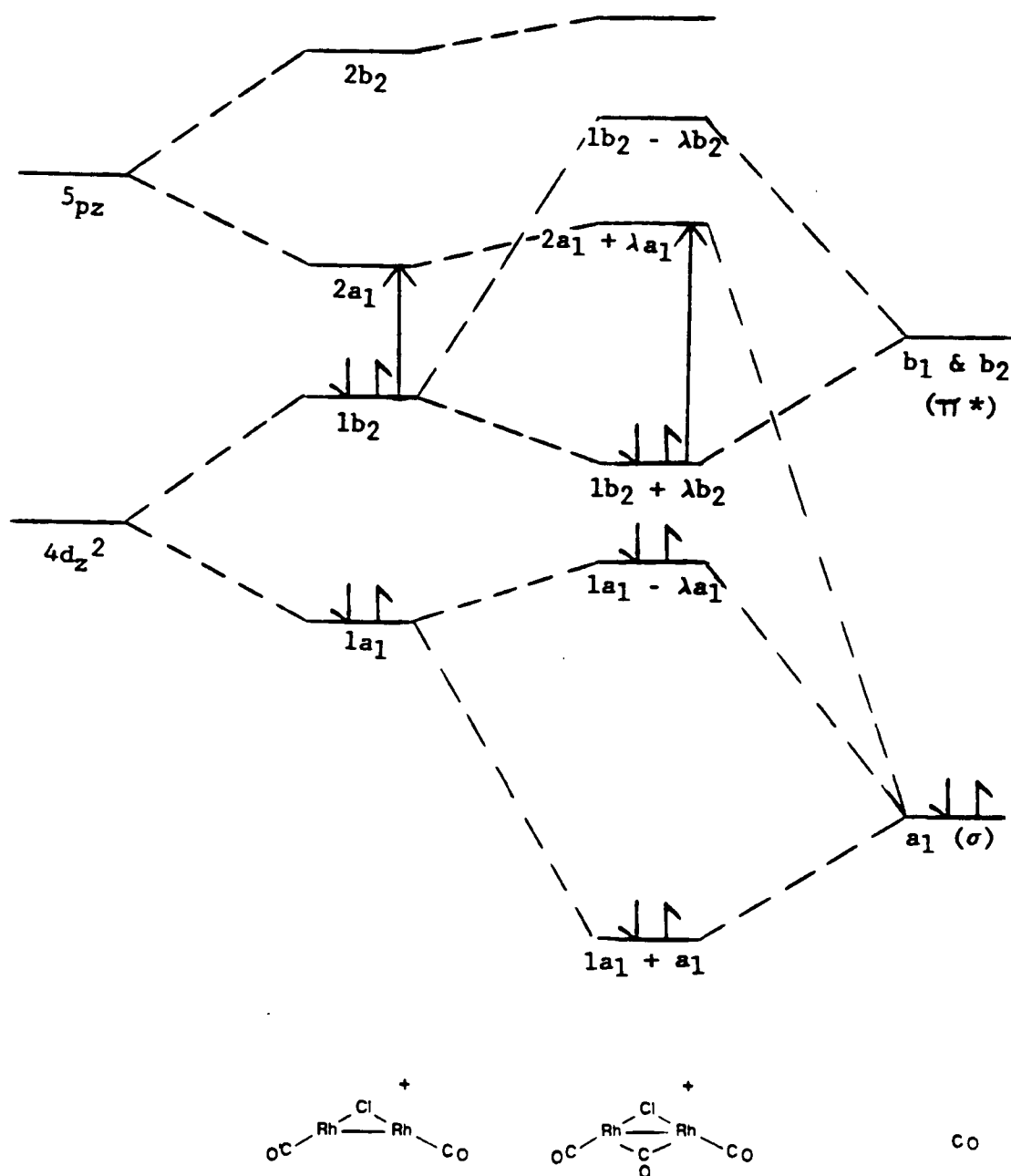
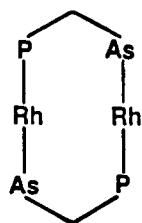


Figure 2. Molecular orbital diagram showing the orbital interaction of carbon monoxide with $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})]^+$.

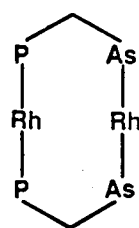
inclined to it by 75.9° (dppm) and 68.5° (dpam) with the chloro ligands folded between the rhodium atoms. The skewing of the planes minimizes the non-bonding contacts between the phenyl rings and the carbonyl and chloro ligands. Another observed geometrical arrangement which helps reduce the interaction between the phenyl rings and equatorial ligands is a trans folding of the methylene groups of the bridging transoid ligands with a displacement of $0.72 \text{ \AA}$ (dppm) and $0.75 \text{ \AA}$ (dpam) from the intraligand Rh-L-L-Rh planes. The Rh-Rh distances of $3.2386 \text{ \AA}$ (dppm) and $3.396 \text{ \AA}$ (dpam) are consistent with no formal metal-metal bond. The larger distance observed for the dpam complex is due to the larger bite size of the arsine ligand.^{9,12} Though not unequivocally diagnostic, the coupling constant $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ from the $^{31}\text{P(H)}$ NMR spectra tends to fall into two broad ranges for metal-metal bonded and non metal-metal bonded diphosphine rhodium dimers. Values of 90-115 Hz are generally observed for complexes with a Rh-Rh bond and those with no Rh-Rh bond are in the range of 125-140 Hz.^{10,13-15}

Although the dppm, dpam, and dapm complexes are isostructural, they do demonstrate differences in their chemical behavior. Before discussing their reactivity, it should be pointed out that two possible structural isomers exist for the dimeric rhodium complexes containing dapm. They are the head-to-head (HH) and head-to-tail (HT) isomers shown below.

In the formation of the double A-frame complex, $[\text{Rh}_2(\mu\text{-L}_2)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})](\text{PF}_6)$ ($\text{L}_2 = \text{dppm, dpam, dapm}$), the bridging carbonyl ligand is more stable for the dppm complex than for the



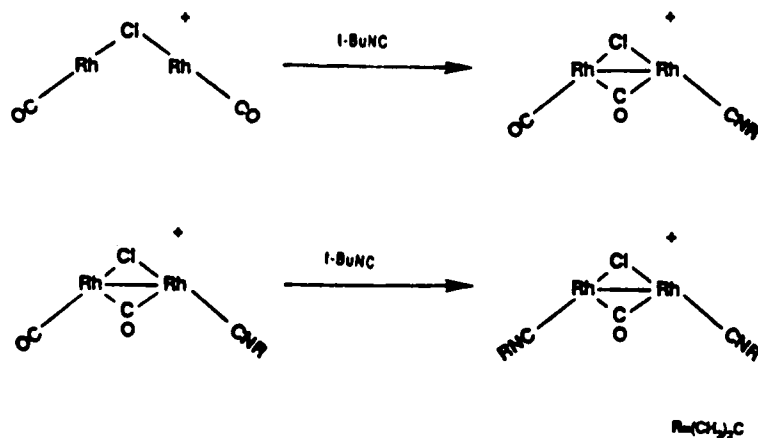
HT



HH

dapm complex¹¹, with the dapm complex being intermediate.¹⁶ This is probably due, in part, to the increase in the metal-metal distance in going from dppm to dpam.¹⁷ However, when the counter ion is tetraphenylborate, (BPh_4^-),⁹ the bridging carbonyl complex that contains dpam is stable in the solid state which could result from packing factors in the solid state in which the BPh_4^- dictates a more stable tricarbonyl complex.

Further studies of the differences in the reactivity of the dppm, dapm and dpam analogs were explored via the addition of *t*-butylisocyanide (*t*-BuNC) to $[\text{Rh}_2(\mu\text{-L}_2)_2(\text{CO})_2(\mu\text{-Cl})](\text{PF}_6)$.^{9,16} When one equivalent is added to the dppm analogue, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})(\text{t-BuNC})(\mu\text{-Cl})(\mu\text{-CO})]^+$ is produced; upon addition of a second equivalent of *t*-BuNC, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Cl})(\mu\text{-CO})]^+$ is formed. These reactions are summarized below. In analogous reactions with the dpam analogue, $[\text{Rh}_2(\mu\text{-dpam})_2\text{Cl}(\text{CO})_2(\text{t-BuNC})]^+$ and $[\text{Rh}_2(\mu\text{-dpam})_2(\text{t-BuNC})_2(\text{Cl})(\text{CO})]^+$ are formed. The product containing one equivalent of *t*-BuNC has carbonyl ligands on different rhodium atoms in a *cis* configuration; for the diisocyanide product, the *t*-BuNC ligands are on the same rhodium atom.¹³ For the HT isomer of the dapm analogue, the same results are obtained as for the dpam



complex. Two carbonyl stretches are observed in the IR spectrum of the dpam and dapm complexes which contain one equivalent of *t*-BuNC. The higher frequency band is assigned to the carbonyl ligand trans to the *t*-BuNC ligand.

Electrochemical studies on tetrakisocyanide face-to-face dimers containing two dppm ligands have been conducted using different solvents.¹⁸ In CH₂Cl₂, the cyclic voltammograms of [Rh₂(μ-dppm)₂(RNC)₄]²⁺ (R = C₄H₉, *i*-C₃H₇, *s*-C₄H₉, C₆H₁₁, *t*-C₄H₉) reveal a one-electron quasi-reversible couple between +0.57 and +0.74 V vs SCE. In CH₃CN, two anodic waves between 0 and +0.5 V are observed with each wave corresponding to a one-electron transfer. If the potential is cycled just past the first anodic wave, a cathodic peak at ca. +0.24 V appears which is similar to what is observed in CH₂Cl₂. Bulk oxidation past the second oxidation wave results in a two-electron process leading to the formation of [Rh₂(μ-dppm)₂(RNC)₄]⁴⁺. When iodide is added to the oxidized solution (R = *n*-C₄H₉), [Rh₂(μ-dppm)₂(*n*-BuNC)₄I₂]²⁺ is produced.

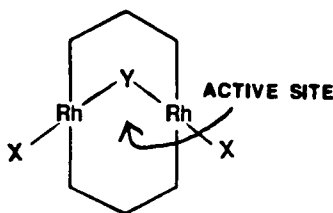
The ability of CH₃CN to facilitate the removal of the second electron led to an investigation of the correlation between the

potential of the second anodic wave and the basicity of certain pyridines.¹⁹ The observation was that a direct correlation exists between the shift to less positive potentials with increasing basicity of the pyridines and a decrease in the cathodic current of the quasi-reversible wave. An interesting result from these experiments was the independence of the first anodic wave on the basicity of the pyridines. This indicates that the pyridines facilitate the removal of the second electron, but not the first.

Other electrochemical studies on transoid dppm complexes were performed by Boyd et al.²⁰ on $[\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-dimen})_2](\text{PF}_6)_2$ (dimen = 1,8 diisocyanomenthane). The cyclic voltammogram of this complex in CH_2Cl_2 reveals two one-electron quasi-reversible couples with the isolation of a stable dinuclear $\text{Rh}(1.5)$ complex when bulk oxidation is performed just past the first anodic wave. Characterization via ESR reveals two components. A resonance with a g-value at 1.99 exhibits a three line pattern due to hyperfine coupling to two equivalent rhodium atoms, and is attributed to magnetic interaction along the Rh-Rh principal magnetic axis. The signal at 2.21 exhibits a five-line pattern due to hyperfine coupling to four equivalent phosphorus atoms, and is attributed to interaction along the Rh_2P_4 principal magnetic axis. A third signal due to the interaction along the $\text{Rh}_2(\text{CN})_4$ principal magnetic axis is not observed and is thought to be masked by the five-line pattern. Chemical reactivity of the mixed-valence species includes a ligand-induced disproportionation reaction. In the presence of chloride,

the mixed-valence dimer undergoes an electron-transfer reaction yielding the parent compound and $\text{Rh}_2(\mu\text{-dppm})_2(\text{dimen})_2\text{Cl}_2$.

As mentioned previously, one reason for the study of face-to-face dimers is their ability to form A-frame complexes.²¹ In the idealized A-frame geometry, the metal atoms are located in a square planar environment and are bridged by "ligand Y" at the apex position. The open site opposite the apex position, called the "active site", is capable of binding small molecules for possible activation during various reactions.²²



Because of the square planar arrangement about the metal atoms and the propensity of d^8 metals to exist in such environments, metal atoms such as Rh(I) are ideally suited for the formation of A-frame complexes.

The first Rh(I) A-frame complex was prepared by C. Kubiak and R. Eisenberg²³ in 1977 by treating a methanolic suspension of $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2$ with Na_2S to produce $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-S})$. This complex exhibits terminal carbonyl stretches at 1910 and 1923 cm^{-1} . Crystal structure analysis confirms the A-frame geometry with the two square planes approximately orthogonal with a dihedral angle between the square planes of 83.3° and a Rh-Rh distance of 3.15 Å. Chemical reactivity includes the displacement of the

carbonyl ligands with isocyanide ligands. The reactivity of the bridging sulphido ligand is exemplified by the addition of an electrophilic reagent, $(\text{OEt}_2\text{R})(\text{PF}_6)$ ($\text{R} = \text{H}, \text{Et}$), yielding mono-alkylated complexes $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-SR})](\text{PF}_6)$ ($\text{R} = \text{H}, \text{Et}$) with an increase in the IR carbonyl bands of about 68 cm^{-1} .

The first example of a rhodium double A-frame complex is one in which the two Rh atoms are simultaneously bridged by a chloride and carbonyl ligand.²⁴ This compound, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-CO})](\text{BPh}_4)$ also demonstrates the reversible binding of the carbonyl ligand in the postulated active site. Crystal structure analysis^{24,25} reveals that the bridging carbonyl and chloride ligands are unsymmetrically bound to each rhodium atom with a Rh-Rh bond length of $2.841 \text{ \AA}$. Although the Rh-Rh bond distance is in the upper limit of a single bond, metal-metal interaction is demonstrated by the observed diamagnetism, a $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 118 Hz, and a high Rh-Rh coupling constant of 128 Hz. The unsymmetrically bound carbonyl ligand is consistent with facile carbonyl exchange and the formation of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})]\text{Cl}$ from $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2$ and CO in polar solvents. The mechanism for the carbonyl exchange was demonstrated using increasing amounts of ^{13}CO together with IR data.^{17,24} It was concluded from the observations that the incoming carbonyl ligand coordinates at a terminal site between the bridging chloride and terminal carbonyl ligand resulting in the formation of an intermediate complex containing three terminal carbonyl ligands. This species then rearranges to form $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})]^+$ with ^{13}CO occupying only a terminal

position. Additional data on the facile carbonyl exchange was obtained via $^{31}\text{P}\{\text{H}\}$ NMR using a CH_2Cl_2 solution containing $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})]^+$ and $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})]^+$. At $-50\text{ }^\circ\text{C}$, the observation of two second order patterns from AA'A''A'''XX' spin systems is consistent with the presence of both dirhodium complexes. As the temperature is raised, broadening occurs with a coalescence of the two signals occurring at room temperature.

Structural analyses of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})]^{+26}$ and $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})]^+$ also reveal that both methylene groups of the dppm ligand are folded over the bridging chloride ligand in a cis orientation. This has come to be a common structural aspect of A-frame and double A-frame complexes. The methylene groups usually bend toward the larger bridging ligand or the more sterically hindered position.^{13-15,25,27-31} This geometry is a result of the positioning of the phenyl rings to minimize non-bonding contacts.

Like CO, SO_2 reversibly coordinates in the active site of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})](\text{BPh}_4)$. It is believed that SO_2^{32} does not attack the terminal site but attacks the bridging site directly as observed with PhN_2 and NO .²⁶ Prolonged treatment of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})](\text{BPh}_4)$ with SO_2 in the presence of chloride ions yields $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-SO}_2)^{14}$ - the first A-frame species with anionic terminal ligands. This complex can also be prepared by treating $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2$ with SO_2 . IR data reveal a terminal attack of SO_2 with the formation of an unsymmetrical intermediate

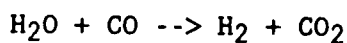
$\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})\text{Cl}(\text{SO}_2)(\mu\text{-Cl})(\mu\text{-CO})$ which then rearranges to give the desired product. Structural analysis reveals a Rh-Rh bond distance of 2.784 Å and a Rh-S-Rh angle of 79.8°. These data together with a $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$ value of 115.5 Hz strongly suggest the presence of a formal Rh-Rh bond. The angle that includes the two Rh atoms and the apex ligand (Rh-Y-Rh) is generally larger^{26,33,34} for complexes which do not contain a formal Rh-Rh bond, and may be more acute than 79.8° for other complexes which contain a formal Rh-Rh bond.²⁴

For the analogous iodo complex, $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-I})\text{I}$, different reactivity is observed.³⁵ When the chloride ligand is replaced by iodide, the rhodium complex does not lose a mole of CO under a stream of dinitrogen. The explanation for this behavior is based on the crystal structure of the chloro species, as well as data that show that the bridging CO converts to a terminal position followed by the loss of the original terminal carbonyl ligand. A crystal structure determination revealed that the terminal carbonyl ligands are bent away from the bridging chloride ligand and that substitution of the larger iodide ligand will increase this effect. This, in turn, will increase the steric hinderance of the intermediate complex which contains three terminal carbonyl ligands resulting in an increase in the energy barrier for the loss of the carbonyl ligand.

Terminal attack of an incoming carbonyl ligand and the fluxional behavior of carbonyl ligands are also demonstrated by halo carboxylate complexes. Treatment of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-O}_2\text{CR})]$ -

(ClO_4) ($\text{R} = \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3, \text{CF}_3$) with CO yields $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-O}_2\text{CR})(\text{ClO}_4)$.³⁶ A direct correlation between the stability of the bridging carbonyl ligand and the increasing electronegativity of the acetate ligand was found. The electronegativity of the halocarboxylate also affects oxidative addition reactions with halogens with the result being a mixture of products. When $\text{R}=\text{H}$ or CH_3 , transannular oxidative-addition products $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{X}_2(\mu\text{-O}_2\text{CR})](\text{ClO}_4)$ ($\text{R} = \text{H}, \text{CH}_3$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) are obtained with a corresponding increase of $40\text{-}60\text{ cm}^{-1}$ in the CO stretching frequency.

The interest in A-frame complexes is due in part to their potential activity as homogeneous catalysts. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-H})]^+$, which is prepared by the treatment of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-CO})]$ with a noncoordinating acid, has been demonstrated by C. Kubiak and R. Eisenberg³⁷ to be a catalyst in the water gas shift reaction:



with the turnover rate being sensitive to pH and proceeding rapidly in the presence of chloride ion. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})]^+$ exhibits catalytic behavior for the hydrogenation of acetylene or alkenes in a hydrogen atmosphere. $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})$ is a catalyst or catalyst precursor in the cyclotrimerization of dimethyl acetylenedicarboxylate (DMA) to hexamethyl mellitate at room temperature in methanol. $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})$ is also a catalyst

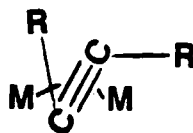
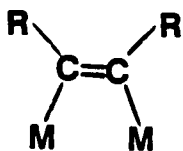
for the hydrogenation of phenylacetylene to styrene under the same conditions as the cyclotrimerization reaction.²⁹ DMA is not hydrogenated due to its highly electron withdrawing nature. In the cyclotrimerization reaction, DMA is believed to insert into the Rh-Cl bonds; if this is the case, the formation of a Rh₂-DMA complex could deactivate the oxidative-addition reaction of hydrogen which is a necessary step in hydrogenation reactions.

The catalytic reaction seen for acetylene and related organic molecules spawned the synthesis of alkyne complexes in the anticipation of understanding the structure and reactivity of hydrocarbons on metal fragments. Terminal alkynes can react with dinuclear metal complexes either as a two- or four-electron donor.^{38,39} The acetylide group ($\text{:C}\equiv\text{CR}^-$) which is quasi-isoelectronic with the carbonyl ligand demonstrates similar modes of coordination.^{30,40-48} The acetylide ion can bridge in either an unsymmetrical manner, σ bound to one metal atom and Π bound to the other metal atom, or in a symmetrical manner, σ bound to both metal atoms.

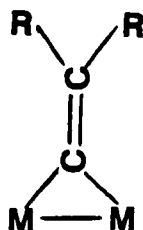


Other modes of coordination of alkynes are seen in the bridging dihapto ($\mu\text{-}\eta^2$) Π complexes in which the C-C bond vector is perpendicular to the M-M vector⁴⁹⁻⁵² or in the cis di-metallated

complex in which the C-C and M-M vectors are parallel and planar.⁵³⁻⁵⁵



Finally, alkynes can react with transition metal complexes to give terminal vinylidene complexes.^{48,49,56}



Acetylenes have been shown to react readily with dinuclear rhodium complexes yielding bridging acetylene complexes. $[\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-DMA})]$ can be prepared by the treatment of DMA with $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2$ or $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})$ under a CO atmosphere.^{29,55} In the latter reaction, as observed for SO_2 ¹³, the incoming carbonyl ligand inserts into the metal-metal bond but is not reversibly bound like SO_2 . When chloride is replaced by iodide, the CO and SO_2 ligands are more tightly bound in the DMA complex - a result of the better π -donating capability of iodide. When HFB¹³ (hexafluoro-2-butyne) is substituted for DMA, the CO and SO_2 ligands are more labile due to the better electron withdrawing properties of HFB.

The loss of a metal-metal bond in forming $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-DMA})$ is suggested by the observed low carbonyl stretching frequency at 1700 cm^{-1} (ketonic carbonyl) and a Rh-C-Rh angle of 116° . Consistent with other dimetallated complexes^{13,53} is the C-C bond distance of $1.32\text{ \AA}$ and the C-C stretching frequency of 1642 cm^{-1} observed for $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-DMA})$.

An attempt to react methylisocyanide with $[\text{Rh}_2(\mu\text{-dppm})_2\text{X}_2(\mu\text{-L})]$ ($\text{X}=\text{Cl}, \text{L}=\text{HFB}, \text{DMA}$; $\text{X}=\text{I}, \text{L}=\text{HFB}$) in experiments similar to those using CO and SO_2 resulted in terminal addition of methylisocyanide.¹³ A crystal structure was obtained for the unsymmetrical complex, $[\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}(\text{MeNC})_2(\mu\text{-HFB})]^+$, in which both methylisocyanide groups are on one metal atom and the chloride ligand is on the other metal atom. The environment around the rhodium atom bound to chloride is similar to the rhodium environment in $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-HFB})$.²⁸ The only difference was found in the Rh-Cl distance of $2.400\text{ \AA}$ in the asymmetric species versus $2.381\text{ \AA}$ for $[\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-HFB})]$ - an effect due to the trans influence of the alkenyl group.⁵⁷ In the asymmetric complex, the chloride ligand is much closer to being trans to the acetylene moiety with a C-Rh-Cl angle of 163° vs 146 and 141° for $[\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-HFB})]$. The same effect is observed for $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-DMA})$ with a Rh-Cl bond distance of $2.44\text{ \AA}$ and a C-Rh-Cl angle of 161° .²⁹ The trans influence of the bridging HFB also affects the Rh-C bond length of the methylisocyanide ligand with the Rh-C bond distance of 2.009 and $1.972\text{ \AA}$ for the isocyanide ligand trans to the acetylene ligand and in line with the Rh-Rh vector, respectively. This

complex also exhibits an unsymmetrically-bridged HFB ligand due to the steric requirements of the methylisocyanide ligands. An unsymmetrical dimetallated acetylene ligand is also observed for $[\text{Rh}_2(\mu\text{-dppm})_2(\text{P}(\text{OMe})_3)(\text{O}_2\text{CMe})(\mu\text{-DMA})]^{58}$ - a result of the trans influence exerted by trimethylphosphite.

The low carbonyl band ca. 1700 cm^{-1} for the bridging carbonyl species, $[\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-DMA})]$, mentioned above has led Cowie and Southern⁵⁵ to consider both rhodium atoms in a formal +3 oxidation state with the carbonyl ligand being dianionic. A low carbonyl band is also observed for $\text{Rh}_2(\mu\text{-dppm})_2\text{Br}_2(\mu\text{-CO})$ in which a ketonic carbonyl ligand is proposed. Although the Rh-Rh distance of $2.756\text{ \AA}$ and a Rh-C-Rh angle of 89.4° are within the range observed for dirhodium complexes containing a Rh-Rh bond, experimental differential electron density determinations⁵⁹ on this and other ketonic complexes have shown no significant electron density along the metal-metal bond axis. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_4(\mu\text{-CO})]^{2+}$ is another complex for which a low bridging carbonyl band is observed.⁹ In this case where the CN stretch can easily be monitored, a ketonic carbonyl does not appear to be reasonable. Since a ketonic carbonyl would imply a formal oxidation state of +2, an expected increase in the CN stretch of $30\text{-}50\text{ cm}^{-1}$ should also be observed relative to $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_4]^{2+}$; however, only a slight change in the CN stretch is observed upon formation of the bridging carbonyl species.

The different modes of coordination observed for some acetylene complexes can result from opposing factors such as the reactivity of the triple bond versus the activation of the

acetylenic C-H bond.⁵⁰ The different reactivities are observed in the reaction of $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-CO})$ with phenylacetylene.⁵⁶ A dihapto mode is prepared by refluxing a 1:1 mixture of the rhodium complex and phenylacetylene. A bridging vinylidene complex, $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-C}_2\text{HPh})$, is prepared by the reaction of $\text{Rh}_2(\mu\text{dppm})_2(\text{CO})_2(\mu\text{-CO})$ with ten equivalents of phenylacetylene in benzene at 25 °C. The latter complex is thermodynamically favored with conversion from the dihapto to the vinylidene complex occurring at 80 °C under a dinitrogen atmosphere.

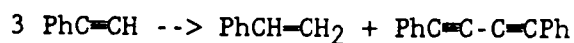
Crystal structure analysis of the dihapto complex reveals a cis arrangement of the dppm ligands and a C-C bond distance of 1.329 Å.⁵⁰ IR analysis reveals the C-C stretch at 1425 cm^{-1} and carbonyl stretches at 1938 and 1923 cm^{-1} . For the A-frame vinylidene complex, trans-dppm ligands and a C-C bond distance of 1.329 Å are observed.

The catalytic behavior of the vinylidene complex, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-C}_2\text{HPh})]$, has been demonstrated by Berry and Eisenberg to include⁵⁶:

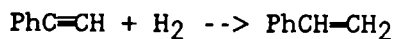
alkyne metathesis;



alkyne disproportionation;



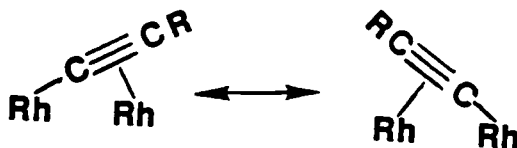
and hydrogenation.



In the hydrogenation reaction, use of deuterium reveals that hydrogenation occurs at the Rh-vinylidene bonds without sufficient exchange to the α position.

Hommeltoft et al.⁶⁰ earlier demonstrated that treatment of $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-H})_2$ with phenylacetylene under a hydrogen atmosphere yields styrene and $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-PhC=CH})$. In this reaction scheme, hydrogenation occurs through cis addition of hydrogen to phenylacetylene.

The σ/π bonding mode of coordinated acetylides is seen in the A-frame complexes $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-C}_2\text{R})](\text{ClO}_4)$ ($\text{R}=\underline{\text{t}}\text{-Bu}$, Ph , H)⁴⁸. These complexes exhibit the typical AA'A'A'XX' pattern in the $^{31}\text{P}(\text{H})$ NMR spectra down to -80°C . This implies that there is a rapid oscillation of the acetylide group between the two rhodium atoms.



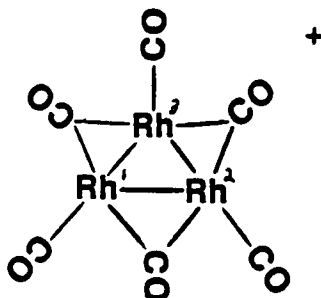
Interaction between the large R group (Phenyl, $\underline{\text{t}}$ -Bu) and the phenyl rings of dppm results in a higher C-C stretching frequency and a shorter C-C bond distance than for the acetylide complex. Nucleophilic attack by LiBHET_3 or NaBH_4 on these complexes results in the formation of the corresponding vinylidene complexes, $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-C}_2\text{HR})$, via attack of the nucleophile on the metal center followed by hydride migration to the β carbon.

Up to this point, all A-frames discussed contained a single atom or small molecule at the bridgehead position. Luis Oro et al.³¹ was one of the first groups to prepare dirhodium A-frame complexes containing a heterocyclic aromatic ligand occupying the bridgehead site. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-L})]^+$ (L = 3,5-dimethylpyrazolate, 3-methylpyrazolate, pyrazolate) were prepared by the treatment of $\text{trans-Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2$ with the appropriate pyrazole in a methanolic KOH solution. Pyrazolate is an anionic five-member ring with two nitrogen donor atoms capable of coordinating to separate rhodium atoms.

These compounds were shown to undergo an oxidative addition reaction upon addition of iodine. These reactions lead to a 65 cm^{-1} increase in the carbonyl stretching frequency. Along with the formation of Rh(II) dimers comes a shortening of the Rh-Rh bond from 3.060 to 2.725 Å, and an increase in the Rh-P bond distance from 2.34 to 2.39 Å for the 3,5-dimethylpyrazolate complex. Luis Oro also prepared two tetramers. These contain two $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2$ units joined either by 3,5,3',5'-tetramethylbipyrazolate or biimidazolate. The $^{31}\text{P}(\text{H})$ NMR spectra of these tetramers reveal chemical shifts and coupling patterns similar to other dinuclear Rh-dppm complexes.

The work of Deraniyagala and Grundy⁶¹ has extended A-frame complexes to contain a metal fragment, $\text{Rh}(\text{CO})_3$, as the apex ligand. Treatment of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-OR})](\text{ClO}_4)$ (R = H, Me, Et) with CO at 2.1 MPa yields a crystalline trinuclear species,

$[\text{Rh}_3(\mu\text{-dppm})_2(\text{CO})_3(\mu\text{-CO})_3](\text{ClO}_4)$ with the basic structural features determined by x-ray analysis.



The IR spectrum reveals six carbonyl bands with the highest frequency band assigned to the terminal carbonyl ligand bound to the unique rhodium atom(3). This carbonyl ligand has also been shown to be the only carbonyl ligand that undergoes rapid exchange with ^{13}CO . The $^{31}\text{P}\{\text{H}\}$ NMR spectrum matches a simulated spectrum of a $\text{AA}'\text{A}''\text{A}''' \text{MXX}'$ spin system. This spin system gives rise to a typical A-frame pattern with each line split into a doublet through coupling to the apex rhodium atom.

The lability of the unique carbonyl ligand was exploited to prepare similar complexes in which $\text{P}(\text{MePh}_2)_3$, PEt_3 , PPh_3 or dppm replaces the terminal carbonyl ligand bound to $\text{Rh}(3)$. In these phosphine complexes ^{13}CO labeled experiments reveal that the 1,3 and 2,3 bridging carbonyl ligands undergo rapid exchange with ^{13}CO . This is unlike the parent compound for which exchange in these positions is evident only after 12 h. For the dppm analogue, $^{31}\text{P}\{\text{H}\}$ NMR studies reveal fluxional behavior of the unique dppm ligand. At ambient temperature, the NMR spectrum resembles that of the parent compound, but at -40°C two different resonances for the dppm ligand

are observed. The $^{31}\text{P(H)}$ NMR signal of the phosphorus atom bound to Rh(3) is split into a doublet-of-doublets with the free phosphorus atom occurring as a doublet at -25 ppm.

Another bridging ligand that has been utilized to support binuclear complexes is the unsymmetrical 2-(diphenylphosphino)pyridine (dppp). Unlike dppm, dpam, and dapm, which are capable of supporting metal-metal distances between 2.1-4.4 Å, dppp limits metal-metal separations to values between 2.2 and 2.8 Å.⁶²⁻⁷⁰ The restricted bite of dppp facilitates the formation of dinuclear complexes containing a metal-metal bond, such that all complexes containing two bridging dppp ligands have a formal metal-metal bond. Thus, these complexes in general will not undergo reactions in which the metal-metal bond is cleaved due to a need to increase the metal-metal separation. Another consequence of the small bite is the skewing of the dppp ligand. This is caused by rotation about the P-C(Py) bond such that a longer metal-metal bond distance can be accommodated.

The skewing of the dppp ligand to accommodate the Rh-Rh distance of 2.612 Å is reflected in the N-Rh-Rh-P torsional angles of 25.1 and 32.0°. Another structural difference is the average Rh-P bond length of 2.21 Å which is shorter than the Rh-P distance in dppm bridged rhodium A-frame complexes.^{29,30} This is a result of a stronger σ donor and weaker π acceptor nitrogen donor atom trans to the phosphorus atom.

Upon formation of the monomer trans-Rh(dppp)₂(CO)Cl⁶², with both dppp ligands phosphorus bound, there is the potential of

chelating a second metal atom to yield a head-to-head dimer. However, addition of $\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4$ to $\text{Rh}(\text{dppp})_2(\text{CO})\text{Cl}$ yields only the head-to-tail A-frame complex, $\text{Rh}_2(\mu\text{-dppp})_2\text{Cl}_2(\mu\text{-CO})$. The formation of the head-to-tail dimer requires that one dppp ligand reorient itself, and emphasizes the mobility of phosphine ligands in binuclear metal-phosphine chemistry.

B. Purpose of Research

The purpose of this research was to investigate the reactivity, spectroscopic and electrochemical properties of novel dirhodium(I) A-frame complexes. Since little is known about the properties of Rh(II) dimers which do not contain four anionic bridging ligands, it was of interest to study dinuclear rhodium(I) complexes that contain dppm and dppp as the transoid-bridging ligands that will undergo reactions forming Rh(II) dimers.

A major focus of this research is the group of trans dppm-dinuclear rhodium complexes that contain pyrazolate derivatives at the bridgehead position with terminal carbonyl and t-butylisocyanide ligands. A primary goal is to determine how ligand modification affects the electron transfer properties of dirhodium(I) complexes and how these modifications dictate the nature of the redox behavior. This study also includes the electrochemical synthesis of several dppm-bridged dirhodium(II) and mixed-valence species, as well as the electrochemical behavior of a certain A-frame complex in the presence of Lewis bases.

This research also focuses on the chemical and electro-chemical behavior of a Rh(I) dimer that contains trans-dppp bridging ligands, and the formation of Rh(II) dimers containing a Rh-Rh bond from this complex. It is also of interest to compare the reactivity of rhodium dimers containing dppp, with its restricted bite size, with complexes containing other bridging ligands such as dppm with the hope of understanding how various geometrical and steric constraints as well as electronic factors affect their corresponding reactivity.

CHAPTER II

EXPERIMENTAL

A. Chemicals

1. Reagents

- a. Rhodium trichloride, trihydrate, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, Johnson Matthey, Inc. Reagent grade $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was used without further purification.
- b. Bis(diphenylphosphino)methane, dppm, Strem Chemicals. Reagent grade dppm was used without further purification.
- c. 1,3-Diphenyltriazine, dpt, Pfaltz & Bauer. Reagent grade dpt was used without further purification.
- d. 2-Chloropyridine, Aldrich. Reagent grade 2-chloropyridine was used without further purification.
- e. Pyridine, Fisher Scientific. Reagent grade pyridine was dried over KOH followed by distillation from BaO.
- f. Hydrazine monohydrate, Aldrich. Reagent grade hydrazine was used without further purification.
- g. Di- μ -chlorobis(dicarbonylrhodium(I), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ is prepared by bubbling ethanol enriched CO through $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (contained in a glass frit) at 100 °C for three hours. The red solid is sublimed at 75 °C and placed in desiccator.
- h. 3,5-Dimethylpyrazole, 35MPzH, Aldrich. Reagent grade 35MPzH was used without further purification.
- i. Pyrazole, PzH, Aldrich. Reagent grade PzH was used without further purification.

- j. 4-Methylpyrazole, 4MPzH, Aldrich. Reagent grade 4MPzH was used without further purification.
- k. 4-Bromo-3,5-Dimethylpyrazole, 4B35MPzH, Pfaltz & Bauer. Reagent grade 4B35MPzH was used without further purification.
- l. 1,2,4-Triazole, TzH, Aldrich. Reagent grade TzH was used without further purification.
- m. Normal butyllithium, n-BuLi, Aldrich. Reagent grade 2.5M n-BuLi was used without further purification.
- n. Diphenylphosphine, Aldrich. Reagent grade diphenylphosphine was used without further purification.
- o. Tertiarybutylisocyanide, t-BuNC, Aldrich. Reagent grade t-BuNC was used without further purification.
- p. Diethylamine, Fisher Scientific. Reagent grade diethylamine was used without further purification.
- q. Mercurous chloride, calomel, Hg₂Cl₂, J.T. Baker. Purified calomel was used as purchased.
- r. Mercury, Hg, Aldrich. Reagent grade 99% Hg was filtered through filter paper before use.
- s. Benzophenone, Fisher. Certified benzophenone was used as purchased.
- t. Sodium metal, Na, Fisher Scientific. Reagent grade Na was used as purchased.
- u. Phosphorus pentoxide, P₂O₅, Mallinckrodt. A.C.S. grade P₂O₅ was used as purchased.
- v. Formaldehyde, Fisher Scientific. Certified A.C.S. formaldehyde was used without further purification.

- w. Sodium hydroxide, NaOH, Fisher Scientific. Certified A.C.S. NaOH was used as purchased.
- x. Potassium hydroxide, KOH, Fisher Scientific. Certified A.C.S. KOH was used as purchased.
- y. 2,4-Pentanedione, acetylacetone, Aldrich. Reagent grade acetylacetone was used without further purification.
- z. Sodium carbonate, Na₂CO₃, Fisher Scientific. Certified A.C.S. anhydrous Na₂CO₃ was used as purchased.
- aa. Magnesium sulfate, MgSO₄, Fisher Scientific. Certified A.C.S. anhydrous MgSO₄ was used as purchased.
- bb. Iodine, I₂, Fisher Scientific. Certified A.C.S. I₂ was used as purchased.
- cc. Bromine, Br₂, Baker Analyzed Reagents. A.C.S. grade Br₂ was used as purchased.
- dd. Phthalazine, phz, Aldrich. Reagent grade phz was used as purchased.
- ee. Potassium permanganate, KMnO₄, Fisher Scientific. Certified A.C.S. KMnO₄ was used as purchased.
- ff. Barium oxide, BaO, Fisher Scientific. Reagent grade anhydrous BaO was used as purchased.
- gg. Activated charcoal, Will Corporation. Reagent grade activated charcoal was used as purchased.
- hh. Sodium hydride, NaH, Aldrich. Reagent grade NaH was used as purchased.
- ii. Nujol, Plough, Inc. Nujol was used after drying over metallic sodium.

- jj. Acetic Acid, CH₃COOH, Fisher Scientific. A.C.S. grade CH₃COOH was used as purchased.
- kk. Nitric acid, HNO₃, Mallinckrodt. A.C.S. grade HNO₃ was used as purchased.
- ll. Sulfuric acid, H₂SO₄, Fisher Scientific. A.C.S. grade H₂SO₄ was used as purchased.
- mm. Perchloric acid, HClO₄, Fisher Scientific. Reagent grade 70% by volume HClO₄ was used as purchased.
- nn. Hydrochloric acid, HCl, Mallinckrodt. A.C.S. grade HCl was used as purchased.
- oo. Tetra-n-butylammonium chloride, TBAC, Aldrich. Reagent grade TBAC was purified by three recrystallizations from acetone-ether followed by drying under vacuum overnight at 70 °C.
- pp. Tetra-n-butylammonium iodide, TBAI, Aldrich. Reagent grade TBAI was purified by three recrystallizations from acetone-ether followed by drying under vacuum overnight at 70 °C.
- qq. Tetra-n-butylammonium bromide, TBAB, Aldrich. Reagent grade TBAB was purified by three recrystallizations from acetone-ether followed by drying under vacuum overnight at 70 °C.
- rr. Tetra-n-butylammonium acetate, TBAAc, Fluka. Reagent grade TBAAc was used as purchased.
- ss. Tetra-n-butylammonium thiocyanate, TBASCN, Fluka. Reagent grade TBASCN was used as purchased.
- tt. 4-(dimethylamino)pyridine, Aldrich. Dimethylaminopyridine was used as purchased.

uu. 3,5-dimethylpyridine, Aldrich. Dimethylpyridine was used as purchased.

vv. Potassium hexafluorophosphate, KPF₆, Aldrich. Reagent grade KPF₆ was used as purchased.

ww. Silver hexafluorophosphate, AgPF₆, Aldrich. Reagent grade AgPF₆ was used as purchased.

xx. Calcium chloride, CaCl₂, Fisher Scientific. Anhydrous CaCl₂ was used as purchased.

yy. Ammonium hexafluorophosphate, NH₄PF₆, Aldrich. Reagent grade NH₄PF₆ was dried in vacuum at 70 °C before use.

zz. Potassium carbonate, K₂CO₃, Fisher Scientific. Anhydrous A.C.S. certified K₂CO₃ was used as purchased.

2. Solvents

a. Tetrahydrofuran, THF, Mallinckrodt. A.C.S. grade THF was freshly distilled from sodium metal-benzophenone before use.

b. Dichloromethane, CH₂Cl₂, Mallinckrodt. A.C.S. grade CH₂Cl₂ was used as purchased. For some electrochemical experiments CH₂Cl₂ was dried over CaCl₂ and distilled from P₂O₅ before use.

c. Acetone, Mallinckrodt. A.C.S. grade acetone was used without further purification. For electrochemical experiments, acetone was dried over molecular sieves followed by distillation.

d. Absolute ethanol, ethanol, U.S. Industrial Chemicals. Ethanol was used as purchased.

e. Methanol, Mallinckrodt. A.C.S. grade methanol was used as purchased.

- f. Hexanes, Mallinckrodt. A.C.S. grade hexanes were used as purchased.
- g. Anhydrous diethyl ether, ether, Mallinckrodt. A.C.S. grade ether was used as purchased.
- h. Chloroform, Mallinckrodt. A.C.S. grade chloroform was used as purchased.
- i. Carbon tetrachloride, Fisher Scientific. A.C.S. grade carbon tetrachloride was used without further purification.
- j. Anhydrous acetonitrile, CH₃CN, Aldrich. Gold Label anhydrous acetonitrile was used as purchased.
- k. Isopropyl alcohol, Fisher Scientific. Reagent grade isopropyl alcohol was used as purchased.
- l. Toluene, Mallinckrodt. A.C.S. grade toluene was used as purchased.
- m. Benzene, Fisher Scientific. Certified A.C.S. grade benzene was used as purchased.
- n. Pentane, Aldrich. Reagent grade pentane was used without further purification.
- o. Propylene carbonate, Aldrich. Reagent grade propylene carbonate was used without further purification.
- p. Distilled water, water, H₂O. Distilled H₂O from the department was used without further purification.
- q. Nitromethane, Fisher Scientific. Certified A.C.S. nitromethane was purified by drying over CaCl₂ followed by distillation.

r. Ligroin, Fisher Scientific. Reagent grade 30-60 ligroin was used as purchased.

3. Supporting Electrolytes

a. Tetra-n-butylammonium nitrate, TBAN, Fluka. Reagent grade TBAN was purified by three recrystallizations from chloroform-ligroin followed by drying under vacuum overnight at 70 °C.

b. Tetraethylammonium perchlorate, TEAP, Eastman Kodak. Reagent grade TEAP was purified by three recrystallizations from water followed by drying under vacuum overnight at 70 °C.

c. Tetra-n-butylammonium tetrafluoroborate, TBAB, Aldrich. Reagent grade TBAB was purified by three recrystallizations from methanol-water followed by drying under vacuum overnight at 70 °C.

d. Tetra-n-butylammonium hexafluorophosphate, TBAH. TBAH was prepared by metathesis of TBAI and KPF₆ in water. TBAH was purified by three recrystallizations from acetone-water followed by drying under vacuum overnight at 70 °C.

4. Gases

a. Argon, Ar, MG Industries. Purified Ar was used without further drying.

b. Nitrogen, N₂, MG Industries. Purified N₂ was used without further drying.

c. Carbon monoxide, CO, MG Industries. Purified CO was used as purchased.

d. Carbon monoxide, ¹³CO, Isotec Inc. 99% enriched ¹³CO was used as purchased.

e. Chlorine, Cl₂. Cl₂ was prepared by introducing HCl into a flask containing KMnO₄. The Cl₂ produced was then bubbled through concentrated H₂SO₄ before reacting with the appropriate complex. Residual Cl₂ was neutralized by bubbling through a concentrated NaOH solution.

B. Cyclic and Pulse Voltammetry

1. Electrodes

A conventional 3-electrode system was employed for all electrochemical studies. The reference electrode was a standard saturated calomel electrode (SCE) which was separated from the bulk solution by a fritted glass tube. The working electrode was a 0.24 cm² platinum button electrode (Beckman) and a 2.76 cm² platinum grid served as the counter electrode.

2. Electrochemical Cells

The cell used for voltammetry was a single compartment cell designed to allow Ar to pass through the solution for degassing or over the solution to ensure continual exclusion of oxygen from the electrolyte solution. All electrochemical measurements using this cell were performed at room temperature.

3. Instrumentation

Electrochemical experiments were performed using two instruments; either a PAR 364 Polarographic Analyzer Potentiostat in conjunction with a sine wave generator designed by Woodward and coworkers⁷¹ with the voltammograms recorded on a Houston

Instruments 2000 Omnigraphic X-Y recorder or a BAS 100 Electrochemical Analyzer with a Houston Instrument DMP-40 series digital plotter. All cyclic voltammograms were recorded at a scan rate of 0.100 V/s.

C. Coulometry

1. Electrodes

A conventional three electrode system was employed for all coulometric studies. The working electrode was a 25 cm² platinum grid; the reference electrode was a standard SCE separated from the bulk solution by a fritted glass tube. The counter electrode was a carbon rod which was placed in a separate compartment from the working and reference electrodes.

2. Electrochemical Cell

A three compartment "H" cell was used for all bulk electrolysis performed at room temperature. The working electrode compartment was fitted with a medium frit bottom which was used for degassing the electrolyte solution with Ar and for convection during electrolysis. The counter electrode compartment was separated from the working and reference electrode by a central compartment fitted on each side by fine frits.

3. Instrumentation

Electrochemical experiments were performed using two instruments; either a PAR 364 Polarographic Analyzer Potentiostat in conjunction with a sine wave generator designed by Woodward

and coworkers⁷¹ with the voltammograms recorded on a Houston Instruments 2000 Omnigraphic X-Y recorder or a BAS 100 Electrochemical Analyzer with a Houston Instrument DMP-400 series digital plotter.

D. Spectroscopy

1. Spectroelectrochemistry

The spectroelectrochemical cell consisted of a platinum button working electrode (Beckman), SCE reference electrode, and a platinum foil counter electrode housed in an open glass container. The reference and counter electrodes were separated from the bulk solution by means of a medium porosity glass frit (Ace Glass). A KBr disk (3cm x 2mm) sealed to the lower end of the cell served as the infrared window (Figure 3).

The potential of the working electrode was controlled by a PAR Model 174A Polarographic Analyzer in conjunction with a PAR Model 175 Universal Programmer. Voltammograms were recorded on an Omnigraphic 2000 X-Y recorder (Houston Instruments).

Infrared spectra were obtained using a Digilab FTS-20E Fourier transform spectrometer (Biorad, Digilab division) equipped with a high-temperature ceramic source and DTGS detector. The reflectance attachment was constructed in this department (UTK) and consisted of two gold-surfaced planar mirrors held in adjustable aluminum mounts.

A dry nitrogen purge was maintained above the degassed solution throughout the entire course of the experiment. The cell

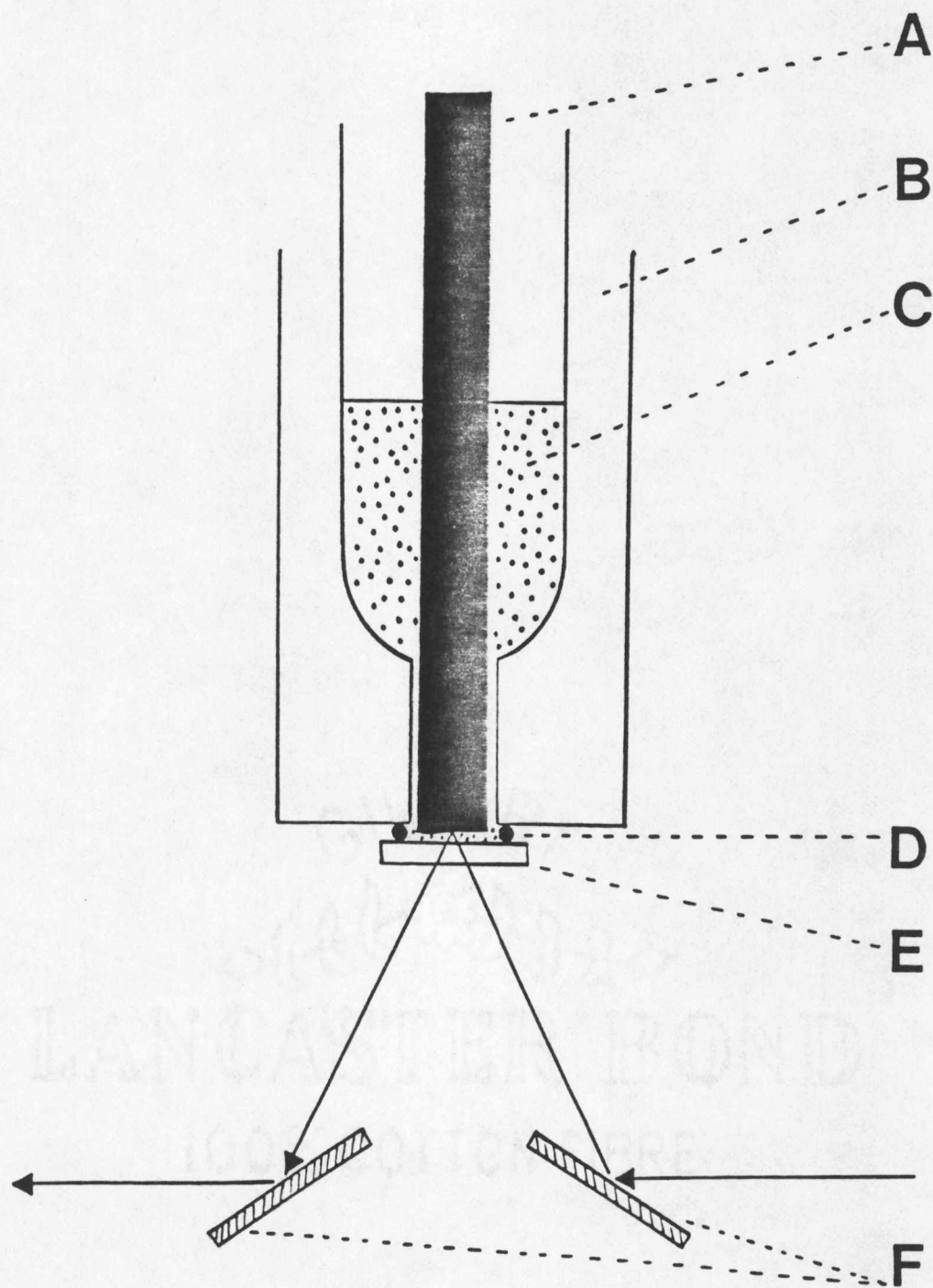


Figure 3. Cell design for infrared spectroelectrochemistry and frozen infrared spectra. Labeled parts: (A) platinum button electrode; (B) coolant compartment; (C) electrolysis solution; (D) O-ring; (E) KBr disk; and (F) gold-surface mirrors.

was mounted in a vertical configuration above the spectrometer's sample compartment, and a thin layer of solution (ca. 1-100 μ m) was isolated by pressing the working electrode firmly against the KBr window. This sample layer was then sampled via external reflectance as described by Foley and Ponds.⁷² Spectra were obtained at rest potential and after the first and second anodic waves of the cyclic voltammogram. Typically, 300-500 scans were collected at an instrumental resolution of 8cm⁻¹ before transformation.

2. Nuclear Magnetic Resonance (NMR)

Proton NMR spectra were recorded on either a Nicolet 200 or JEOL FX90Q Fourier transform spectrophotometers with tetramethylsilane (TMS) as the internal reference. ³¹P(H) NMR spectra were recorded on a JEOL FX90Q Fourier transform spectrophotometer operating at 36.21 MHz with 85% phosphoric acid as the external reference. ¹³C(H) spectra were recorded on a JEOL FX90Q operating at 22.51 MHz with TMS as the internal reference.

For ¹H NMR the instrument was locked on the deuterated solvent of (CD₃)₂CO or CD₂Cl₂. For all other spectra, the instrument was locked on the deuterium signal of (CD₃)₂CO contained in a sealed 5 mm tube placed in a 10 mm sample tube. All solvents were degassed with Ar prior to use.

3. Infrared Spectroscopy (IR)

IR spectra were obtained using either a Perkin-Elmer 1330 Infrared spectrometer or a Digilab FTS-20 C/V Fourier transform spectrometer. Spectra of solid samples were obtained using nujol

mulls between thin polyethylene sheets or as KBr pellets. Solution IR spectra were obtained using CH_2Cl_2 in liquid cells equipped with NaCl plates.

Frozen-solution IR spectra were obtained using the cell design shown in Figure 3, with the outer jacket filled with liquid N_2 to freeze the sample. External reflectance sampling was employed to obtain the spectra.

4. Near Infrared Spectroscopy (NIR)

A Cary 17D spectrophotometer was used to obtain all room-temperature NIR spectra. Quartz cells (Markson) of 1.0 cm path length were used with degassed CH_2Cl_2 as the solvent. Spectra were recorded using the solvent in the reference beam.

5. Ultraviolet-Visible Spectroscopy (UV-Vis)

A Varian Cary 219 spectrophotometer was used to obtain all room-temperature UV-Vis spectra. Quartz cells (Fisher Scientific) of 1.0 cm path length were used with degassed CH_2Cl_2 as the solvent. Spectra were recorded using the solvent in the reference beam.

6. Electron Spin Resonance (ESR)

A JEOL JES-PE-1X spectrometer or a Bruker ER 200D-SRC K-band was used to obtain all ESR spectra. Room-temperature spectra were obtained with CH_2Cl_2 as the solvent. A 4:1 CH_2Cl_2 /toluene solvent mixture was used for spectra that were obtained at low temperatures.

E. Miscellaneous

An Orion Research chloride-ion electrode (model no. 94-17) was used in conjunction with an Orion Research double junction reference electrode (model no. 90-02) to test for chloride ions.

F. Elemental Analysis

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

G. Preparation of Ligands

1. 2-(diphenylphosphino)pyridine, dppp.

dppp was prepared by the method of Mann and Watson.⁷³

M.P., 84 °C.

2. 3,4,5-tribromopyrazole, 345BPzH.

345BPzH was prepared by the method used by Upjohn Co.⁷⁴

M.P., 183-184 °C.

3. 3,5,3',5'-tetramethyl-4,4'-bipyrazole, bPzH₂.

bPzH₂ was prepared by the method of Mosby.⁷⁵

M.P., 299-300 °C.

4. 4,4'-methylenebis(3,5-dimethylpyrazole), mbPzH₂.

mbPzH₂ was prepared by the method of Knoevenagel.⁷⁶

M.P., 277-278 °C.

5. 1,3,4,5-d₄-pyrazole, d₃-PzD. d₃-PzD was prepared by the method of Troitskaya, Konevskaya, Vinokurov and Tyulin.⁷⁷

Mass spectrometric data: 23.6% 1,3,4,5-d₃-PzD; 37% 1,3,4-d₂-PzD & 1,4,5-d₂-PzD.

H. Preparation of Rhodium Complexes

1. Dicarbonyl- μ -chlorobis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})](\text{PF}_6)$.

A procedure similar to that used by Mague and Sanger¹⁷ was adapted to prepare 1. The only alteration was the use of NH_4PF_6 in place of sodium tetraphenylborate.

IR (nujol mull): $\nu_{(\text{CO})}$, $1994\text{ cm}^{-1}(\text{sh})$ and $1978\text{ cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 18.9 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 114.7 Hz.

2. Dicarbonyldichlorobis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I), $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2$.

The procedure of Mague and Mitchner⁷⁸ (Method A) was used to prepare 2.

IR (nujol mull): $\nu_{(\text{CO})}$, $1971\text{ cm}^{-1}(\text{s})$. $^{31}\text{P}(\text{H})$ NMR: δ , 19.2 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 119.6 Hz.

3. Bis(t-butylisocyanide)- μ -carbonyl- μ -chlorobis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-CO})(\mu\text{-Cl})](\text{PF}_6)$.

The procedure of Mague and DeVries⁹ was used to prepare 3.

IR (nujol mull): $\nu_{(\text{CN})}$, $2125\text{ cm}^{-1}(\text{s})$; $\nu_{(\text{CO})}$, $1813\text{ cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$.

4. μ -Carbonyl- μ -chlorodichlorobis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-CO})\text{Cl}_2(\mu\text{-Cl})](\text{PF}_6)$.

The procedure of Tinsley⁷⁹ was used to prepare 4. Fifty mL of a CH_2Cl_2 solution of 2 (141 mg, 0.13 mmol) containing 0.1 M TBAH and TBAC (356 mg, 1.28 mmol) was oxidized at +0.60 V via controlled-potential electrolysis. The volume of the reddish-brown oxidized solution was reduced to ca. 5 mL, to which 50 mL of CH_3OH was added. The resulting suspension was stirred for 24 h during which time it turned from brown to green. The solid was filtered and stirred overnight in 10 mL of CH_2Cl_2 . The green solid was filtered and dried in vacuo. The product was recrystallized from CH_2Cl_2 . Yield 70%.

IR (nujol mull): $\nu_{(\text{CO})}$, 1794 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$, UV-Vis: $[\lambda_{\text{max}}, \text{nm}(\epsilon)]$: 346 (16,000); 310 (32,000). $^{31}\text{P}(\text{H})$ NMR: δ , 9.80 ppm; $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$, 97.7 Hz.

5. μ -Carbonyldichlorobis[2-(diphenylphosphino)pyridine-N:P]dirhodium(I), $[\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-CO})\text{Cl}_2]$.

The procedure of Balch⁸⁰ was used to prepare 5.

IR (nujol mull): $\nu_{(\text{CO})}$, 1801 cm^{-1} .

6. ^{13}CO analogue of 5, $[\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-CO})\text{Cl}_2]$.

Compound 6 was prepared by the procedure used for 5 using 99% enriched ^{13}CO to prepare $[\text{Rh}(\text{CO})_2\text{Cl}]_2$.

IR (nujol mull): $\nu_{(\text{CO})}$, 1763 $\text{cm}^{-1}(\text{s})$.

7. Carbonyltrichloro- μ -nitratobis[2-(diphenylphosphino)pyridine-N:P]dirhodium(II), $[\text{Rh}_2(\mu\text{-dppp})_2\text{COCl}_3(\mu\text{-NO}_3)]$.

Fifty mL of a CH_2Cl_2 solution of 5 (120 mg, 0.14 mmol) containing 0.1 M TBAN and TBAC (0.201g, 0.72 mmol) was oxidized at +1.0 V. After oxidation was complete, the solution was washed with copious amounts of water to remove TBAN and TBAC. The CH_2Cl_2 layer was reduced in volume on a rotary evaporator, and a green solid was precipitated with ether and recrystallized from CH_2Cl_2 /ether. Yield 70%.

IR (nujol mull): $\nu_{(\text{CO})}$, 2054 cm^{-1} (s). UV-Vis: $[\lambda_{\text{max}}$, nm(ϵ)] : 573 (680), 474 (2,200), 350 (21,360). $^{31}\text{P}\{\text{H}\}$ NMR: Two doublets-of-doublets; δ , 33.0 and 28.7 ppm; $^1\text{J}_{(\text{Rh-P})}$, 114.7 Hz (downfield doublet) and 119.6 Hz (upfield doublet); $^2\text{J}_{(\text{Rh-P})}$, 17.1 Hz.

8. ^{13}C analogue of 7, $[\text{Rh}_2(\mu\text{-dppp})_2\text{COCl}_3(\mu\text{-NO}_3)]$.

This compound was prepared according to the procedure for 7 using 6 instead of 5.

IR (nujol mull): $\nu_{(\text{CO})}$, 2006 cm^{-1} . $^{31}\text{P}\{\text{H}\}$ NMR: Doublet-of-doublet; δ , 28.8 ppm; pseudo-doublet-of-triplets; δ , 33.0 ppm; $^1\text{H}_{(\text{Rh-P})}$, 117.2 Hz (pseudo triplet) and 120.1 Hz (doublet); $^2\text{J}_{(\text{C-P})}$, 14.6 Hz; $^2\text{J}_{(\text{Rh-P})}$, 14.6 Hz.

9. Carbonyltrichloro- μ -chlorobis[2-diphenylphosphino)pyridine-N:P]dirhodium(II), $[\text{Rh}_2(\mu\text{-dppp})_2\text{CO}(\mu\text{-Cl})\text{Cl}_3]$.

a. Method 1. Fifty mL of a CH_2Cl_2 solution of 5 (120 mg, 0.14 mmol) containing 0.1 M TBAH and TBAC (200.6 mg, 0.72 mmol) was oxidized at +0.85 V. After oxidation the solution was stripped

to dryness on a rotary evaporator and stirred in acetone overnight. The brown precipitate was filtered and dried in vacuo. Yield 80%.

b. Method 2. Excess Cl_2 was bubbled through a stirred 125 mL solution of CH_2Cl_2 containing 5 (100 mg, 0.12 mmol) at -77°C . The solution was then allowed to reach room temperature and stirred for an additional hour. The resulting solution was stripped to dryness and acetone was added to precipitate the product. The precipitate was filtered and dried in vacuo. Yield 80%.

IR (nujol mull): $\nu_{(\text{CO})}$, $2044\text{ cm}^{-1}(\text{s})$ and $1805\text{ cm}^{-1}(\text{m})$.
 $^{31}\text{P}(\text{H})$ NMR (-25°C): Two doublets-of-doublets; δ , 29.7 and 23.2 ppm;
 $^1\text{J}_{(\text{Rh-P})}$, 117.2 Hz (downfield doublet) and 109.9 Hz (upfield doublet); $^2\text{J}_{(\text{Rh-P})}$, 14.6 Hz (downfield multiplet) and 12.2 Hz (upfield multiplet). UV-Vis [λ_{max} , nm(ϵ)]: 705 (137); 497 (683), 363 (7,587); 304 (6015); 163 (17,880). Anal. calcd. for $\text{C}_{35}\text{H}_{28}\text{Cl}_4\text{N}_2\text{OP}_2\text{-Rh}_2\cdot(\text{CH}_3)_2\text{CO}$: C, 47.53; H, 3.57; N, 2.92; Cl, 14.77. Found: C, 47.57; H, 3.94; N, 3.23; Cl, 14.58.

10. ^{13}CO analogue of 9. $[\text{Rh}_2(\mu\text{-dppp})_2\text{CO}(\mu\text{-Cl})\text{Cl}_3]$.

This compound was prepared according to the procedure used for 9 (Method 1) using 6 instead of 5.

IR (nujol mull): $\nu_{(\text{CO})}$, $1998\text{ cm}^{-1}(\text{s})$ and $1765\text{ cm}^{-1}(\text{m})$.
 $^{31}\text{P}(\text{H})$ NMR: $^2\text{J}_{(\text{P-C})}$, 12.2 Hz. $^{31}\text{P}(\text{H})$ NMR (-25°C): Doublet-of-doublet; δ , 29.7 ppm; psuedo-doublet-of-triplets; δ , 23.0 ppm;
 $^1\text{J}_{(\text{Rh-P})}$, 117.2 Hz (doublet) and 107.4 Hz (pseudo-triplet); $^2\text{J}_{(\text{C-P})}$, 12.2 Hz; $^2\text{J}_{(\text{Rh-P})}$, 14.6 Hz.

11. Dicarbonyltetrachlorobis[2-(diphenylphosphino)pyridine-N:P]-dirhodium(II). [Rh₂(μ-dppp)₂(CO)₂Cl₄].

CO was bubbled through a stirred CH₂Cl₂ solution containing 9 (96.4 mg, 0.10 mmol) for 10 min., during which it changed from brown to orange. The solution was reduced via a rotary evaporator to ca. 20 mL, and an orange solid precipitated upon addition of ether. Recrystallization from CH₂Cl₂/ether afforded a crystalline orange solid in 90% yield.

IR (nujol mull): $\nu_{(\text{CO})}$, 2066 cm⁻¹(s) and 2039 cm⁻¹(m).
³¹P(H) NMR: δ , 22.4 ppm; $^1J_{(\text{Rh-P})}$, 109.9 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 460 (3,000); 415 (8,400); 325 (8,800); 264 (23,600).

Anal. calcd. for C₃₆H₂₈Cl₄N₂O₂Rh₂·1/2CH₂Cl₂: C, 45.07; H, 3.01; N, 2.88; Cl, 18.22. Found: C, 45.40; H, 3.23; N, 2.79; Cl, 17.94.

12. Bis(t-butylisocyanide)tetrachlorobis[2-(diphenylphosphino)-pyridine-N:P]dirhodium(II). [Rh₂(μ-dppp)₂(t-BuNC)₂Cl₄].

To a 100 mL CH₂Cl₂ solution of 9 or 11 (0.11 mmol), t-BuNC (95 mg, 1.14 mmol) was added dropwise with a color change from brown to orange. After stirring for 1 hr. the solution was reduced via a rotary evaporator to ca. 50 mL with an orange solid obtained upon addition of a 1:1 ether/hexanes solution. Yield 70%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2189 cm⁻¹(s) and 2218 cm⁻¹(w).
UV-Vis [λ_{max} , nm(ϵ)]: 481 (2400); 368sh (9100); 343 (13,000); 264 (23,000). Anal. calcd. for C₄₄H₄₆Cl₄N₄P₂Rh₂: C, 50.79; H, 4.46; N, 5.38; Cl, 13.63. Found: C, 49.58; H, 5.01; N, 5.67; Cl, 12.30.

13. Bis(t-butylisocyanide)dichloro-μ-chlorobis[2-(diphenylphosphino)pyridine-N:P]dirhodium(II) hexafluorophosphate, [Rh₂(μ-dppp)₂(t-BuNC)₂(μ-Cl)Cl₂](PF₆).

To a 150 mL 4:1 CH₂Cl₂/MeOH solution of 12 (55.2 mg, 0.05 mmol), NH₄PF₆ (22 mg, 0.13 mmol) in methanol was added. After stirring for 1 h, the resulting solution was reduced to ca. 40 mL with a yellow-orange solid obtained upon addition of a 1:1 ether/hexanes solution.

IR (nujol mull): $\nu_{(\text{CN})}$, 2183 cm⁻¹(s), 2222 cm⁻¹(w) and 2122 cm⁻¹(w); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m). ³¹P{H} NMR: δ , 25.3 ppm. [¹J_(Rh-P) + ^xJ_(Rh-P)], 112.3 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 474 (2300); 343 (19,000); 265 (33,000). Anal. calcd. for C₄₄H₄₆Cl₃F₆N₄P₃Rh₂: C, 45.96; H, 4.03. Found: C, 45.56; H, 4.42.

14. Carbonyl-μ-chlorotrichlorobis[μ-methylenebis(diphenylphosphine)-P:P']dirhodium(II), [Rh₂(μ-dppm)₂CO(μ-Cl)Cl₃].

a. Method 1. Fifty mL of a CH₂Cl₂ solution of 2 (121 mg, 0.11 mmol) containing 0.1 M TBAN and TBAC (167 mg, 0.55 mmol) was oxidized at +0.75 V via controlled-potential electrolysis. The volume of the brown oxidized solution was reduced to 30 mL and the solution was washed with three 100 mL portions of water. The CH₂Cl₂ was reduced in volume and a brown solid was obtained upon addition of ether. The product was recrystallized from CH₂Cl₂/ether. Yield 75%.

b. Method 2. The procedure outlined by Janke was used to obtain 14.

IR (nujol mull): $\nu_{(\text{CO})}$, 2025 $\text{cm}^{-1}(\text{s})$. UV-Vis [λ_{max} , $\text{nm}(\epsilon)$]: 383 (11,500); 303 (23,600).

15. Dicarbonyl- μ -chlorodichlorobis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}_2](\text{PF}_6)$.

CO was passed over an acetone solution of 4 (80 mg, 0.06 mmol) until the solution turned bright orange. The resulting solution was reduced to ca. 15 mL via a rotary evaporator. A 1:1 ether/hexanes solution was added to precipitate an orange solid. The product was recrystallized from CH_2Cl_2 /ether/hexanes. The yield is quantitative.

IR (nujol mull): $\nu_{(\text{CO})}$, 2058 $\text{cm}^{-1}(\text{s})$ and 2025 $\text{cm}^{-1}(\text{sh})$; $\nu(\text{PF}_6^-)$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , $\text{nm}(\epsilon)$]: 444 (2,200); 362 (31,000); 317 (41,000). $^{31}\text{P}(\text{H})$ NMR: δ , 11.3 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 75.7 Hz. Anal. calcd. for $\text{C}_{52}\text{H}_{44}\text{F}_6\text{O}_2\text{P}_5\text{Rh}_2 \cdot \text{CH}_2\text{Cl}_2$: C, 46.57; H, 3.39; Cl, 12.97. Found: C, 46.75; H, 3.44; Cl, 12.30.

16. Dicarbonyltetrachlorobis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II), $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_4]$.

A CH_2Cl_2 solution of 14 (50 mg, 0.04 mmol) was bubbled with CO for 5 min., during which the solution turned from brown to orange. The product precipitated upon addition of a 1:1 mixture of ether/hexanes. The yield is quantitative.

IR (nujol mull): $\nu_{(\text{CO})}$, 2041 $\text{cm}^{-1}(\text{s})$. UV-Vis [λ_{max} , $\text{nm}(\epsilon)$]: 454 (4,800); 383 (20,000); 304, (37,000). $^{31}\text{P}(\text{H})$ NMR: δ , 8.76 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 87.9 Hz.

17. Bis(t-butylisocyanide)- μ -chlorodichlorobis[μ -methylenebis-diphenylphosphine-P:P']dirhodium(II) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Cl})\text{Cl}_2](\text{PF}_6)$.

a. Method 1. To 0.173 mmol of 4 or 15 in 150 mL of acetone two equivalents (0.35 mmol) of t-BuNC were added. After stirring for ca. 0.5 hr, the solution was reduced in volume on a rotary evaporator. A solid precipitated when a 1:1 mixture of ether/ligroin was slowly added. The product was recrystallized from an acetone/ether/hexanes mixture. Yield 81%.

b. Method 2. The procedure outlined by Tinsley¹² was used to prepare 17.

IR (nujol mull): $\nu_{(\text{CN})}$, 2172 $\text{cm}^{-1}(\text{s})$ and 2153 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 2.8 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 84.5 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 499 (1300); 371 (26,000); 309 (25,000); 269 (23,000). Anal. calcd. for $\text{C}_{60}\text{H}_{62}\text{Cl}_3\text{F}_6\text{P}_5\text{Rh}_2$: 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.

18. Dicarbonyl- μ -pyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Pz})](\text{PF}_6)$.

a. Method 1. The procedure outlined by Janke⁸¹ was used to prepare 18. Pyrazole (44.0 mg, 0.65 mmol) dissolved in freshly distilled THF was treated with n-BuLi (0.65 mmol, 0.26 mL). Drop-wise addition of the lithium pyrazolate solution to 1 (760.3 mg, 0.63 mmol) in THF resulted in a color change from yellow to red. While the solution stirred a precipitate formed. The volume was

reduced and a red crystalline solid was collected by filtration.

b. Method 2. Pyrazole (91.3 mg, 1.34 mmol) dissolved in methanol was treated with a methanol solution containing 0.1 M KOH (17.34 mL, 1.73 mmol). Dropwise addition of the potassium pyrazolate solution to 1 (1.061g, 0.88 mmol) in methanol resulted in a color change from yellow to red. After the solution stirred for 1 h, the volume was reduced and a precipitate formed. The red crystalline solid was filtered and dried in vacuo.

IR (nujol mull): $\nu_{(\text{CO})}$, 1988 $\text{cm}^{-1}(\text{s})$ and 1967 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 19.25 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 128.9 Hz.

19. Dicarbonyl- μ -3,5-dimethylpyrazolato- $\text{N:N'bis}[\mu$ -methylenebis-diphenylphosphine- P:P']dirhodium(I) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-35MPz})](\text{PF}_6)$.

Compound 19 was prepared by the same procedure used to synthesize 18 using 3,5-dimethylpyrazole (0.1304g, 1.36 mmol), KOH (0.08 M, 20.17 mL), and 1 (1.084 g, 0.90 mmol).

IR (nujol mull): $\nu_{(\text{CO})}$, 1975 $\text{cm}^{-1}(\text{s})$ and 1962 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 22.79 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 129.4 Hz.

20. Dicarbonyl- μ -4-methylpyrazolato- $\text{N:N'bis}[\mu$ -methylenebis(diphenylphosphine)- P:P']dirhodium(I) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4MPz})](\text{PF}_6)$.

Compound 20 was prepared by the same procedure used to synthesize 18 using 4-methylpyrazole (0.107 g, 1.30 mmol), KOH (0.1 M, 15.3 mL) and 1 (1.0423 g, 0.86 mmol).

IR (nujol mull): $\nu_{(\text{CO})}$, $1984\text{ cm}^{-1}(\text{s})$ and $1973\text{ cm}^{-1}(\text{m})$;
 $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$.

21. Dicarbonyl- μ -1,2,4-triazolato- $\text{N}:\text{N}'$ bis[μ -methylenebis(di-phenylphosphine)- $\text{P}:\text{P}'$]dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Tz})](\text{PF}_6)$.

Compound 21 was prepared by the same method used to synthesize 18 using triazole (0.1039 g, 1.5 mmol), KOH (0.064 M, 30 mL), and 1 (1.1913 g, 0.98 mmol).

IR (nujol mull): $\nu_{(\text{CO})}$, $1991\text{ cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 23.47 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 127.0 Hz.

22. Dicarbonyl- μ -4-bromo-3,5-dimethylpyrazolato- $\text{N}:\text{N}'$ bis[μ -methylenebis(diphenylphosphine)- $\text{P}:\text{P}'$]dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4B35MPz})](\text{PF}_6)$.

Compound 22 was prepared by the procedure used to synthesize 18 using 4-bromo-3,5-dimethylpyrazole (95.5 mg, 0.55 mmol), KOH (36.0 mg, 0.64 mmol) and 1 (0.440 g, 0.36 mmol), with an orange solid being obtained. Yield 96%.

IR (nujol mull): $\nu_{(\text{CO})}$, $1989\text{ cm}^{-1}(\text{s})$ and $1979\text{ cm}^{-1}(\text{m})$;
 $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 22.1 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 129.4 Hz. UV-Vis [λ_{max} , nm(ϵ)]:
492 (12,700); 295sh (13,700).

23. Dicarbonyl- μ -3,4,5-tribromopyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-345BPz})](\text{PF}_6)$.

The procedure outlined for 18 was used to prepare 23 using 3,4,5-tribromopyrazole (0.367 g, 1.19 mmol), KOH (82 mg, 1.46 mmol) and 1 (0.9635 g, 0.80 mmol). An orange solid was obtained. Yield 97%.

IR (nujol mull): $\nu_{(\text{CO})}$, 1992 $\text{cm}^{-1}(\text{s})$ and 1975 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 20.6 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 126.9 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 480 (11,900); 385sh (1,800); 366 (2,500).

24. Bis(t-butyliisocyanide)- μ -pyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Pz})](\text{PF}_6)$.

Compound 18 (0.3062 g, 0.25 mmol) was dissolved in 100 mL of degassed acetone under an inert atmosphere. While the acetone solution was stirred, t-BuNC (41.0 mg, 0.49 mmol) was added dropwise. After being stirred for 0.5 h, the solution was reduced in volume via a rotary evaporator. A red crystalline solid was obtained with the addition of a 1:1 mixture of ether/hexanes. Yield 93%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2118 $\text{cm}^{-1}(\text{s})$ and 2066 $\text{cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, 893 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 22.7 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 141.6 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 514 (14,300); 332sh (6,300); 300 (15,000).

25. Bis(t-butylisocyanide)- μ -4-methylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)$.

Compound 25 was prepared by the same procedure used to synthesize 24 using 20 (0.2328 g, 0.18 mmol) and t-BuNC (30.8 mg, 0.37 mmol). A purple crystalline solid was obtained. Yield 90%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2120 $\text{cm}^{-1}(\text{s})$ and 2065 $\text{cm}^{-1}(\text{sh})$; $\nu(\text{PF}_6^-)$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 22.4 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 144.0 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 514 (10,200); 331sh (4,000); 301 (10,700).

26. Bis(t-butylisocyanide)- μ -3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)$.

Compound 26 was prepared by the same procedure used to synthesize 24 using 19 (0.3093 g, 0.24 mmol) and t-BuNC (40.5 mg, 0.49 mmol). A purple crystalline solid was obtained. Yield 90%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2110 $\text{cm}^{-1}(\text{s})$ and 2096 $\text{cm}^{-1}(\text{sh})$; $\nu(\text{PF}_6^-)$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 20.3 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 139.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 505 (9,600); 332sh (6900); 305 (14,000).

27. Bis(t-butylisocyanide)- μ -1,2,4-triazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Tz})](\text{PF}_6)$.

Compound 27 was prepared by the same procedure used to synthesize 24 using 21 (0.3047 g, 0.24 mmol) and t-BuNC (40.7 mg, 0.49 mmol). A red crystalline solid was obtained. Yield 70%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2124 $\text{cm}^{-1}(\text{s})$ and 2064 $\text{cm}^{-1}(\text{sh})$;
 $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 21.7 ppm;
 $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 139.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]:
 504 (14,637); 365sh (2500); 335sh (5,350); 300 (12,711).

28. Bis(t-butylisocyanide)- μ -4-bromo-3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4B35MPz})](\text{PF}_6)$.

Compound 28 was prepared by the same procedure used to synthesize 24 using 22 (0.2309 g, 0.17 mmol) and t-BuNC (28.4 mg, 0.34 mmol). An orange solid was obtained. Yield 88%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2106 $\text{cm}^{-1}(\text{s})$ and 2070 $\text{cm}^{-1}(\text{sh})$;
 $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 19.8 ppm;
 $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 139.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]:
 505 (12,300); 331 (5,600); 304 (13,800).

29. Bis(t-butylisocyanide)- μ -3,4,5-tribromopyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-345BPz})](\text{PF}_6)$.

Compound 29 was prepared by the same procedure used to synthesize 24 using 23 (0.2068 g, 0.14 mmol) and t-BuNC (23.2 mg, 0.28 mmol). A purple-pink solid was obtained. Yield 85%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2114 $\text{cm}^{-1}(\text{s})$ and 2070 $\text{cm}^{-1}(\text{sh})$;
 $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 18.0 ppm;
 $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 139.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]:
 492 (13,300); 370sh (3,400); 305 (15,500).

30. Carbonyl(t-butylisocyanide)- μ -pyrazolato-N:N'bis[μ -methylene-bis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate.
[Rh₂(μ -dppm)₂(CO)(t-BuNC)(μ -Pz)](PF₆).

Compound 18 (0.2439 g, 0.20 mmol) was dissolved in 150 mL of degassed acetone under an inert atmosphere. To the stirred solution, t-BuNC (16.3 mg, 0.20 mmol) was added dropwise. After the mixture stirred for 1 h, the product was precipitated slowly with degassed ether. The resulting solution was filtered and a purple-red crystalline solid was obtained. Yield 55%.

IR (nujol mull): $\nu_{(\text{CO})}$, 1960 cm⁻¹(s); $\nu_{(\text{CN})}$, 2122 cm⁻¹(s); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m). UV-Vis [λ_{max} , nm(ϵ)]: 505 (13,300); 296 (11,500).

31. Carbonyl(t-butylisocyanide)- μ -4-methylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophosphate. [Rh₂(μ -dppm)₂(CO)(t-BuNC)(μ -4MPz)](PF₆).

Compound 31 was prepared by the same procedure used to synthesize 30 using 20 (0.2464 g, 0.20 mmol) and t-BuNC (16.3 mg, 0.20 mmol). A purple-red crystalline solid was obtained. Yield 63%.

IR (nujol mull): $\nu_{(\text{CO})}$, 1972 cm⁻¹(s); $\nu_{(\text{CN})}$, 2122 cm⁻¹(s); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m). UV-Vis [λ_{max} , nm(ϵ)]: 506 (12,100); 422 (1,700); 362sh (4,100); 298 (12,600).

32. Carbonyl(t-butylisocyanide)- μ -3,5-dimethylpyrazolato-N:N'bis-
[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophos-
phate, $[\text{Rh}_2(\mu\text{dppm})_2(\text{CO})(t\text{-BuNC})(\mu\text{-35MPz})](\text{PF}_6)$.

Compound 32 was prepared by the same procedure used to
synthesize 30 using 19 (0.1613 g, 0.13 mmol) and t-BuNC (10.6 mg,
0.13 mmol). An orange crystalline solid was obtained. Yield 55%.

IR (nujol mull): $\nu_{(\text{CO})}$, $1975\text{ cm}^{-1}(\text{s})$; $\nu_{(\text{CN})}$, $2133\text{ cm}^{-1}(\text{s})$;
 $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]:
496 (13,200); 370sh (3,200); 298 (12,800).

33. Carbonyl(t-butylisocyanide)- μ -1,2,4-triazolato-N:N'bis[μ -
methylenebis(diphenylphosphine)-P:P']dirhodium(I) hexafluorophos-
phate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})(t\text{-BuNC})(\mu\text{-Tz})](\text{PF}_6)$.

Compound 33 was prepared by the same procedure used to
synthesize 30 using 21 (0.2385 g, 0.19 mmol) and t-BuNC (15.9 mg,
0.19 mmol). A red crystalline solid was obtained. Yield 55%.

IR (nujol mull): $\nu_{(\text{CO})}$, $1979\text{ cm}^{-1}(\text{s})$; $\nu_{(\text{CN})}$, $2129\text{ cm}^{-1}(\text{s})$;
 $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]:
493 (14,000); 366 (2,800); 294 (11,300).

34. Bis(t-butylisocyanide)- μ -pyrazolato-N:N'bis[μ -methylenebis-
(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-}$
 $\text{dppm})_2(t\text{-BuNC})_2(\mu\text{-Pz})](\text{PF}_6)_2$.

a. Method 1. Fifty mL of a CH_2Cl_2 solution of 24 (0.1327 g,
0.10 mmol) containing 0.1 M TBAH was oxidized at +0.30 V via con-
trolled potential electrolysis. The resulting green oxidized solu-
tion was stripped to dryness and 50 mL of CH_3OH was added. After
stirring overnight, the solution was filtered to yield a green

crystalline solid. The product was recrystallized from CH₂Cl₂/ether/hexanes and dried in vacuo. Yield 80%.

b. Method 2. 0.39 M H₂SO₄ (0.30 mL, 0.12 mmol) in THF was added dropwise to a THF solution containing 24 (78.3 mg, 0.06 mmol) and TBAH (45 mg, 0.12 mmol). After being stirred for 1 h, the solvent was stripped off. The resulting green residue was dissolved in CH₂Cl₂ and a green crystalline solid was obtained with the addition of a 1:1 mixture of ether/hexanes.

IR (nujol mull): $\nu_{(\text{CN})}$, 2172 cm⁻¹(s) and 2161 cm⁻¹(m); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m). UV-Vis [λ_{max} , nm(ϵ)]: 580 (1,200); 427 (38,000); 384sh (3,400). NIR [λ_{max} , nm(ϵ)]: 845 (780); 994 (380).

35. Bis(t-butylisocyanide)- μ -4-methylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate. [Rh₂(μ -dppm)₂(t-BuNC)₂(μ -4MPz)](PF₆)₂.

Compound 35 was prepared by the same procedures used to synthesize 34. Using Method 1, 25 (0.1365 g, 0.10 mmol) was oxidized at +0.25 V. Using Method 2, 25 (84.6 mg, 0.06 mmol), TBAH (48 mg, 0.12 mmol) and 1 M H₂SO₄ (0.13 mL, 0.13 mmol) reacted to give a green crystalline solid. Yield 78%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2172 cm⁻¹(s); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 839 cm⁻¹(m). UV-Vis [λ_{max} , nm(ϵ)]: 562 (1,110); 427 (26,000); 384sh (3,400). NIR [λ_{max} , nm(ϵ)]: 849 (630); 990 (310).

36. Bis(t-butylisocyanide)- μ -3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$.

Compound 36 was prepared by the same procedures used to synthesize 34. Using Method 1, 26 (0.1295 g, 0.09 mmol) was oxidized at +0.25 V. Using Method 2, 26 (59.3 mg, 0.04 mmol), TBAH (33 mg, 0.08 mmol) and 1 M H_2SO_4 (0.08 mL, 0.09 mmol) reacted to give a green crystalline solid. Yield 81%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2168\text{ cm}^{-1}(\text{s})$ and $2166\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]: 583 (1,200); 429 (24,700); 386sh (3,400). NIR [λ_{max} , nm(ϵ)]: 862 (850); 996 (370).

37. Bis(t-butylisocyanide)- μ -4-bromo-3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate, $\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4B35MPz})](\text{PF}_6)_2$.

Compound 37 was prepared by the same procedures used to synthesize 34. Using Method 1, 28 (0.1353 g, 0.09 mmol) was oxidized at +0.35 V. Using Method 2, 28 (50.6 mg, 0.03 mmol), TBAH (27 mg, 0.07 mmol) and 1 M H_2SO_4 (0.07 mL, 0.07 mmol) reacted to give a green crystalline solid. Yield 81%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2174\text{ cm}^{-1}(\text{s})$ and $2156\text{ cm}^{-1}(\text{m})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]: 580 (1,400); 427 (33,700). NIR [λ_{max} , nm(ϵ)]: 856 (680); 994 (300).

38. Bis(t-butylisocyanide)- μ -3,4,5-tribromopyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-345BPz})](\text{PF}_6)_2$.

Compound 38 was prepared by the same procedures used to synthesize 34. Using Method 1, 29 (0.1383 g, 0.09 mmol) was oxidized at +0.45 V. Using Method 2, 29 (85.3 mg, 0.06 mmol), TBAH (45 mg, 0.12 mmol) and 1 M H_2SO_4 (0.12 mL, 0.12 mmol) reacted to give a green crystalline solid. Yield 65%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2174\text{ cm}^{-1}(\text{s})$ and $2158\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]: 604 (1,300); 476sh (2,500); 422 (19,000); 398 (4,200). NIR [λ_{max} , nm(ϵ)]: 853 (730); 980 (325).

39. Bis(t-butylisocyanide)- μ -1,2,4-triazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Tz})](\text{PF}_6)_2$.

Compound 39 was prepared by the same procedure used to synthesize 34. Compound 27 (0.1304 g, 0.10 mmol) was oxidized at +0.4 V and afforded a green crystalline solid. Yield 75%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2176\text{ cm}^{-1}(\text{s})$ and $2171\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]: 575 (1,900); 421 (29,000); 335 (1,950). NIR [λ_{max} , nm(ϵ)]: 846 (750); 988 (375).

40. Bis(t-butylisocyanide)dichloro- μ -pyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)_2$.

a. Method 1. Fifty mL of a CH_2Cl_2 solution of 24

(0.1114 g, 0.08 mmol) containing 0.1 M TBAH and TBAC (0.115 g, 0.41 mmol) was oxidized at +0.2 V via controlled-potential electrolysis. The volume of the oxidized yellow-orange solution was reduced to ca. 10 mL, to which 50 mL of CH₃OH was added. The resulting solution was stirred overnight during which time a precipitate formed. The yellow-orange solid was filtered, recrystallized from CH₂Cl₂/ether/hexanes and dried in vacuo. Yield 73%.

b. Method 2. Chlorine gas was bubbled through a stirred CH₂Cl₂ solution of 24 (82.4 mg, 0.06 mmol) at -77 °C. The resulting yellow solution was allowed to reach room temperature and stirred for an additional hour. The volume of the solution was reduced to ca. 25 mL and a 1:1 mixture of ether/hexanes was added to precipitate a yellow-orange solid. The solid was collected by filtration and recrystallized from CH₂Cl₂/ether/hexanes. Yield 75%.

c. Method 3. Fifty mL of a CH₂Cl₂ solution of 24 (74.9 mg, 0.05 mmol) containing 0.1M TBAH and TBAAc (83.5 mg, 0.28 mmol) was oxidized at +0.10 V via controlled-potential electrolysis. The volume of the yellow-orange oxidized solution was reduced to ca. 10 mL, to which 50 mL of CH₃OH was added. The resulting solution was stirred overnight during which time a precipitate formed. An orange solid was collected by filtration and dried in vacuo.

IR (nujol mull): $\nu_{(\text{CN})}$, 2176 cm⁻¹(s) and 2164 cm⁻¹(sh); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m). UV-Vis [λ_{max} , nm(ϵ)]: 464 (2,200); 370 (20,900); 322 (19,000); 252 (34,800). ³¹P{H} NMR: δ , 4.3 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 92.8 Hz. Anal. calcd. for

$C_{63}H_{65}Cl_2F_6N_4P_5Rh_2 \cdot CH_2Cl_2$: C, 50.95; H, 4.47; Cl, 9.39. Found: C, 51.57; H, 4.59; Cl, 9.35.

41. Bis(t-butylisocyanide)dichloro- μ -4-methylpyrazolato-N:N'bis-
[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluoro-
phosphate, $Rh_2(\mu-dppm)_2(t-BuNC)_2Cl_2(\mu-4MPz)](PF_6)$.

Compound 41 was prepared by Methods 1 and 2 used to synthesize 40. Using Method 1, 25 (79.2 mg, 0.06 mmol) and TBAC (81 mg, 0.03 mmol) were oxidized at +0.20 V. Using Method 2, 25 (88.5 mg, 0.06 mmol) afforded an orange-yellow solid. Using Method 3, 12 M HCl (0.005 mL, 0.06 mmol) diluted in methanol was added dropwise to a methanol solution of 25 (39.9 mg, 0.03 mmol). The resulting orange solution was reduced in volume with the formation of an orange precipitate. The product was collected by filtration and dried in vacuo.

IR (nujol mull): $\nu_{(CN)}$, 2176 cm^{-1} (s) and 2165 cm^{-1} (sh); $\nu_{(PF_6^-)}$, 839 cm^{-1} (s) and 557 cm^{-1} (m). UV-Vis [λ_{max} , nm(ϵ)]: 451sh (2,150); 370 (15,250); 322 (15,500); 299sh (31,000). $^{31}P(H)$ NMR: δ , 4.2 ppm; [$^1J_{(Rh-P)} + ^xJ_{(Rh-P)}$], 90.3 Hz.

42. Bis(t-butylisocyanide)dichloro- μ -3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[Rh_2(\mu-dppm)_2(t-BuNC)_2Cl_2(\mu-35DMPz)](PF_6)$.

Compound 42 was prepared by the same procedure (Method 1) used to synthesize 40. Compound 26 (67.9 mg, 0.05 mmol) and TBAC (68 mg, 0.25 mmol) were oxidized at +0.15 V and an orange-yellow solid was obtained. Yield 65%.

IR (nujol mull): $\nu_{(CN)}$, 2176 cm^{-1} (s) and 2172 cm^{-1} (sh);

$\nu(\text{PF}_6^-)$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]:
464 (1960); 379 (24,900); 320 (20,500); 261sh (32,900). $^{31}\text{P}\{\text{H}\}$
NMR: δ , 10.7 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 92.7 Hz.

43. Bis(t-butylisocyanide)dichloro- μ -1,2,4-triazolato-N:N'bis-
[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluoro-
phosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Tz})](\text{PF}_6)$.

Compound 43 was prepared by the same procedure (Method 1) used to synthesize 40. Compound 27 (81.7 mg, 0.06 mmol) and TBAC (67 mg, 0.24 mmol) were oxidized at +0.20 V, and an orange-yellow solid was obtained. Yield 70%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2180\text{ cm}^{-1}(\text{s})$ and $2156\text{ cm}^{-1}(\text{m})$;
 $\nu(\text{PF}_6^-)$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]:
457 (2,100); 368 (20,600); 293 (19,000); 254sh (26,700). $^{31}\text{P}\{\text{H}\}$
NMR: δ , 1.3 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 90.3 Hz.

44. Bis(t-butylisocyanide)dibromo- μ -pyrazolato-N:N'bis[μ -
methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophos-
phate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Br}_2(\mu\text{-Pz})](\text{PF}_6)$.

a. Method 1. Fifty mL of a CH_2Cl_2 solution of 24 (0.1016 g, 0.07 mmol) containing 0.1 M TBAH and TBAB (0.194 g, 0.60 mmol) was oxidized at +0.20 V via controlled-potential electrolysis. The volume of the orange oxidized solution was reduced to ca. 10 mL, to which 50 mL of CH_3OH was added. The resulting solution was stirred overnight during which time a precipitate formed. The orange crystalline solid was collected by filtration, recrystallized from CH_2Cl_2 /ether/hexanes, and dried in vacuo. Yield 77%.

b. Method 2. To a 150 mL stirred CH_2Cl_2 solution of 24

(0.1003 g, 0.07 mmol) at -77°C , Br_2 (0.012 g, 0.07 mmol) in 50 mL of CCl_4 was slowly added via a transfer needle. The resulting orange solution was allowed to reach room temperature and stirred for an additional 1.5 h. The volume was reduced to ca. 25 mL and ether/hexanes added to precipitate an orange crystalline solid. The orange solid was collected by filtration, recrystallized from CH_2Cl_2 /ether/hexanes and dried in vacuo. Yield 90%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2176\text{ cm}^{-1}(\text{s})$ and $2164\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 5.2 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 92.8 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 473sh (4,000); 405 (20,000); 314 (19,000); 256 (30,000).

Anal. calcd. for $\text{C}_{63}\text{H}_{65}\text{Br}_2\text{F}_6\text{N}_4\text{P}_5\text{Rh}_2$: N, 3.70; Br, 10.56. Found: N, 3.52; Br, 9.99.

45. Bis(t-butylisocyanide)dibromo- μ -4-methylpyrazolato-N,N'-bis-[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Br}_2(\mu\text{-4MPz})](\text{PF}_6)$.

Compound 45 was prepared by the same procedures used to synthesize 44. Using Method 1, 25 (46.7 mg, 0.03 mmol) and TBAB (0.108 g, 0.34 mmol) were oxidized at +0.2 V. Using Method 2, 25 (64.9 mg, 0.05 mmol) and Br_2 (7.6 mg, 0.05 mmol) afforded an orange crystalline solid. Yield 90%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2176\text{ cm}^{-1}(\text{s})$ and $2168\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 5.2 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 92.8 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 478sh (3,900); 408 (28,000); 314 (16,000); 254 (39,000).

46. Bis(t-butylisocyanide)dibromo- μ -3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Br}_2(\mu\text{-35MPz})](\text{PF}_6)$.

Compound 46 was prepared by the same procedures used to synthesize 44. Using Method 1, 26 (83.3 mg, 0.06 mmol) and TBAB (97.2 mg, 0.30 mmol) were oxidized at +0.2 V. Using Method 2, 26 (92.3 mg, 0.07 mmol) and Br_2 (10.7 mg, 0.07 mmol) afforded an orange crystalline solid. Yield 80%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2168\text{ cm}^{-1}(\text{s})$ and $2156\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}\{\text{H}\}$ NMR: δ , 8.4 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 92.8 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 483 (2,900); 408 (44,000); 324 (22,000); 265 (48,000).

47. Bis(t-butylisocyanide)dibromo- μ -1,2,4-triazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Br}_2(\mu\text{-Tz})](\text{PF}_6)$.

Compound 47 was prepared by the same procedures used to synthesize 44. Using Method 1, 27 (89.5 mg, 0.07 mmol) and TBAB (85.2 mg, 0.26 mmol) were oxidized at +0.30 V. Using Method 2, 27 (81.3 mg, 0.06 mmol) and Br_2 (9.6 mg, 0.06 mmol) afforded an orange crystalline solid. Yield 90%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2172\text{ cm}^{-1}(\text{s})$ and $2166\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}\{\text{H}\}$ NMR: δ , 1.9 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 90.3 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 472sh (4,400); 400 (33,000); 303 (22,000); 258 (29,000).

48. Bis(t-butylisocyanide)dibromo- μ -3,4,5-bromopyrazolato-N:N'-bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Br}_2(\mu\text{-345BPz})](\text{PF}_6)$.

Compound 48 was prepared by the same procedures used to synthesize 44. Using Method 1, 29 (96.4 mg, 0.06 mmol) and TBAB (97.8 mg, 0.30 mmol) were oxidized at +0.1 V. Using Method 2, 29 (0.1045 g, 0.07 mmol) and Br_2 (42.0 mg, 0.53 mmol) afforded an orange solid. Yield 80%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2165\text{ cm}^{-1}(\text{s})$ and $2155\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}\{\text{H}\}$ NMR: δ , 7.9 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 92.8 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 474sh (2,500); 408 (32,800); 320 (25,000); 271 (44,500).

49. Bis(t-butylisocyanide)diiodo- μ -pyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{I}_2(\mu\text{-Pz})](\text{PF}_6)$.

a. Method 1. Fifty mL of a CH_2Cl_2 solution of 24 (0.1059 g, 0.08 mmol) containing 0.1 M TBAH and TBAI (0.145 g, 0.39 mmol) was oxidized at +0.2 V via controlled-potential electrolysis. The volume of the brown oxidized solution was reduced to ca. 10 mL, to which 50 mL of CH_3OH was added. The resulting solution was stirred overnight during which time a precipitate formed. The brown crystalline solid was collected by filtration, recrystallized from CH_2Cl_2 /ether/hexanes and dried in vacuo. Yield 77%.

b. Method 2. To a 150 mL stirred CH_2Cl_2 solution of 24 (0.1093 g, 0.08 mmol) at -77°C , I_2 (20.5 mg, 0.08 mmol) in 50 mL

of CCl_4 was slowly added via a transfer needle. The resulting brown solution was allowed to reach room temperature and stirred for an additional 1.5 h. The volume was reduced to ca. 25 mL with ether/hexanes added to precipitate a brown crystalline solid. The solid was collected by filtration, recrystallized from CH_2Cl_2 /ether/hexanes and dried in vacuo. Yield 82%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2164\text{ cm}^{-1}(\text{s})$ and $2133\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 4.6 ppm; $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$, 95.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 507sh (17,000); 463 (32,000); 320 (14,000); 257 (46,000).

50. Bis(t-butylisocyanide)diiodo- μ -4-methylpyrazolato-N:N'-bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{I}_2(\mu\text{-4MPz})](\text{PF}_6)$.

Compound 50 was prepared by the same procedures used to synthesize 49. Using Method 1, 25 (94.4 mg, 0.07 mmol) and TBAI (0.126 g, 0.34 mmol) were oxidized at +0.20 V. Using Method 2, 25 (92.4 mg, 0.07 mmol) and I_2 (17.2 mg, 0.07 mmol) gave a brown crystalline solid. Yield 85%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2164\text{ cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 4.6 ppm; $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$: 95.3 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 512 (16,000); 464 (30,000); 328 (13,000); 256 (45,000).

51. Bis(t-butylisocyanide)diiodo- μ -3,5-dimethylpyrazolato-N:N'-bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{I}_2(\mu\text{-35MPz})](\text{PF}_6)$.

Compound 51 was prepared by the same procedures used to

synthesize 49. Using Method 1, 26 (86.0 mg; 0.06 mmol) and TBAI (0.115 g, 0.31 mmol) were oxidized at +0.15 V. Yield 60%. Using Method 2, 26 (88.0 mg, 0.06 mmol) and I₂ (16.2 mg, 0.06 mmol) gave a brown crystalline solid. Yield 90%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2156 cm⁻¹(s); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m). ³¹P(H) NMR: δ , 4.7 ppm; [¹J_(Rh-P) + ^xJ_(Rh-P)], 95.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 521 (20,000); 464 (47,000); 365 (17,000); 326 (19,000); 267 (65,000).

52. Bis(t-butylisocyanide)diiodo- μ -1,2,4-triazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. [Rh₂(μ -dppm)₂(t-BuNC)₂I₂(μ -Tz)](PF₆).

Compound 52 was prepared by the same procedures used to synthesize 49. Using Method 1, 27 (71.4 mg, 0.05 mmol) and TBAI (97.4 mg, 0.26 mmol) were oxidized at +0.25 V. Using Method 2, 27 (88.5 mg, 0.06 mmol) and I₂ (16.6 mg, 0.06 mmol) gave a brown crystalline product. Yield 77%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2156 cm⁻¹(s) and 2172 cm⁻¹(s); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m). ³¹P(H) NMR: δ , 2.7 ppm; [¹J_(Rh-P) + ^xJ_(Rh-P)], 90.3 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 511 (12,000); 462 (25,000); 332 (3,800); 259 (33,000).

53. Bis(t-butylisocyanide)dithiocyanato- μ -pyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. [Rh₂(μ -dppm)₂(t-BuNC)₂(SCN)₂(μ -Pz)](PF₆).

Fifty mL of a CH₂Cl₂ solution of 24 (0.1093 g, 0.08 mmol) containing 0.1 M TBAH and TBASCN (0.1214 g, 0.40 mmol) was oxidized at +0.20 V via controlled-potential electrolysis. The

volume of the oxidized red-orange solution was reduced to ca. 10 mL to which 50 mL of CH₃OH was added. The resulting solution was stirred overnight during which time a precipitate formed. The orange crystalline solid was collected by filtration, recrystallized from CH₂Cl₂/ether/hexanes and dried in vacuo. Yield 95%.

IR (nujol mull): $\nu_{(\text{BuNC})}$, 2176 cm⁻¹(s); $\nu_{(-\text{NCS})}$, 2045 cm⁻¹(m); $\nu_{(-\text{SCN})}$, 2091 cm⁻¹(m). UV-Vis [λ_{max} , nm(ϵ)]: 450 (35,000); 407sh (22,000); 309 (23,000); 266 (59,000).

54. Bis(t-butylisocyanide)dithiocyanato- μ -4-methylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. [Rh₂(μ -dppm)₂(t-BuNC)₂(SCN)₂(μ -4MPz)](PF₆).

Compound 54 was prepared by the same procedure used to synthesize 53 by oxidizing 25 (86.5 mg; 0.06 mmol) and TBASCN (57.1 mg, 0.19 mmol) at +0.15 V. An orange solid was obtained. Yield 60%.

IR (nujol mull): $\nu_{(\text{BuNC})}$, 2176 cm⁻¹(s); $\nu_{(-\text{SCN})}$, 2091 cm⁻¹(m); $\nu_{(-\text{NCS})}$, 2056 cm⁻¹(m).

55. Bis(t-butylisocyanide)dithiocyanato- μ -3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. [Rh₂(μ -dppm)₂(t-BuNC)(SCN)₂(μ -35MPz)](PF₆).

Compound 55 was prepared by the same procedure used to synthesize 53 by oxidizing 26 (83.7 mg, 0.06 mmol) and TBASCN (54.6 mg, 0.18 mmol) at +0.10 V. An orange solid was obtained. Yield 60%.

IR (nujol mull): $\nu_{(\text{BuNC})}$, 2176 cm⁻¹(m); $\nu_{(-\text{SCN})}$, 2091 cm⁻¹(m); $\nu_{(-\text{NCS})}$, 2060 cm⁻¹(s).

56. Bis(t-butylisocyanide)dithiocyanato- μ -1,2,4-triazolato-N:N'-bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{SCN})_2(\mu\text{-Tz})](\text{PF}_6)$.

Compound 56 was prepared by the same procedure used to synthesize 53 by oxidizing 27 (86.7 mg, 0.06 mmol) and TBASCN (81.7 mg, 0.17 mmol) at +0.30 V. An orange solid was obtained. Yield 60%.

IR (nujol mull): $\nu_{(\text{BuNC})}$, 2187 $\text{cm}^{-1}(\text{s})$, $\nu_{(-\text{NCS})}$, 2044 $\text{cm}^{-1}(\text{s})$ and 2046 $\text{cm}^{-1}(\text{sh})$; $\nu_{(-\text{SCN})}$, 2097 $\text{cm}^{-1}(\text{wsh})$.

57. Bis{dicarbonylbis[μ -methylenebis(diphenylphosphine)-P:P']-dirhodium(I)}- μ -3,5,3',5'-tetramethyl-4,4'-bipyrazolato-N:N':N':N''':hexafluorophosphate, $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2]_2(\mu\text{-bpz})\}(\text{PF}_6)_2$.

Bpy (46.7 mg, 0.24 mmol) dissolved in methanol was treated with a methanol solution containing 0.079 M KOH (7.56 mL, 0.60 mmol). Dropwise addition of the potassium bipyrazolate solution to 7 (0.5943 g, 0.49 mmol) in methanol resulted in a color change from yellow to red. After stirring for 2 h, the volume was reduced with the formation of a precipitate. The purple-red solid was filtered and dried in vacuo. Yield 91%.

IR (nujol mull): $\nu_{(\text{CO})}$, 1985 $\text{cm}^{-1}(\text{s})$ and 1971 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 22.2 ppm; $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$, 129.4 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 492 (22,000); 352sh (5,200); 300 (23,400). Anal. calcd. for $\text{C}_{114}\text{H}_{100}\text{F}_{12}\text{N}_4\text{O}_4\text{P}_{10}\text{Rh}_4$: C, 53.88; H, 3.97; N, 2.20. Found: C, 52.73; H, 4.08; N, 2.10.

58. Bis[dicarbonylbis[μ -methylenebis(diphenylphosphine)-P:P']-dirhodium(I)]- μ -4,4'-methylenebis(3,5-dimethylpyrazolato-N:N':N'':N''') hexafluorophosphate, $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2](\mu\text{-mbpy})\}(\text{PF}_6)_2$.

Compound 58 was prepared by the same procedure used to synthesize 57 using mbpy (49.1 mg, 0.24 mmol), 0.079 M KOH (7.23 mg, 0.57 mmol) and 7 (0.5820 g, 0.48 mmol). An orange solid was obtained. Yield 92%.

IR (nujol mull): $\nu_{(\text{CO})}$, 1962 $\text{cm}^{-1}(\text{s})$, 1971 $\text{cm}^{-1}(\text{m})$, 1990 $\text{cm}^{-1}(\text{m})$ and 2006 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 19.7 ppm; [$^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}$], 139.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 491 (50,000); 356sh (11,000); 302 (55,000). Anal. calcd. for $\text{C}_{115}\text{H}_{102}\text{F}_{12}\text{N}_4\text{O}_4\text{P}_{10}\text{Rh}_4$: C, 54.05; H, 4.02; N, 2.19. Found: C, 53.99; H, 4.12; N, 2.00.

59. Bis[bis(t-butylisocyanide)bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I)]- μ -3,5,3',5'-tetramethyl-4,4'-bipyrazolato-N:N':N'':N''') hexafluorophosphate, $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{-bpz})\}(\text{PF}_6)_2$.

Compound 57 (0.1720 g, 0.07 mmol) was dissolved in 100 mL of degassed acetone under an inert atmosphere. While the acetone solution was stirred, t-BuNC (22.5 mg, 0.27 mmol) was added dropwise. After the mixture stirred for 0.5 h, the product was precipitated with a 1:1 mixture of degassed ether/hexanes. The resulting solution was filtered to afford a red crystalline solid. Yield 90%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2100 $\text{cm}^{-1}(\text{s})$ and 2072 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 19.5 ppm;

$[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, 141.6 Hz. UV-Vis $[\lambda_{\text{max}}, \text{nm}(\epsilon)]$:
509 (21,000); 309 (29,700).

60. Bis(bis(t-butylisocyanide)bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(I)]- μ -4,4'-methylenebis(3,5-dimethylpyrazolato)-N:N':N'':N''' hexafluorophosphate, $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{-mbpz})\}(\text{PF}_6)_2$.

Compound 60 was prepared by the same procedure used to synthesize 59 using t-BuNC (22.6 mg, 0.27 mmol) and 58 (0.1733 g, 0.07 mmol). A red crystalline solid was obtained. Yield 90%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2110 $\text{cm}^{-1}(\text{s})$ and 2075 $\text{cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 19.7 ppm; $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, 139.2 Hz. UV-Vis $[\lambda_{\text{max}}, \text{nm}(\epsilon)]$:
511 (11,800); 432 (5,000); 308 (23,700).

61. Bis(bis(t-butylisocyanide)bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5)] μ -3,5,3',5'-tetramethyl-4,4'-bipyrazolato-N:N':N'':N''' hexafluorophosphate, $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{-bpz})\}(\text{PF}_6)_4$.

Fifty mL of a CH_2Cl_2 solution of 59 (0.1229 g, 0.04 mmol) containing 0.1 M TBAH was oxidized at +0.25 V via controlled potential electrolysis. The resulting green oxidized solution was stripped to ca. 10 mL and 50 mL of methanol was added. The suspension stirred for 0.5 h at which time it was filtered to yield a green solid. The product was recrystallized from CH_2Cl_2 /ether/hexanes and dried in vacuo. Yield 75%.

IR (nujol mull): $\nu_{(\text{CN})}$, 2164 $\text{cm}^{-1}(\text{s})$ and 2154 $\text{cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. UV-Vis $[\lambda_{\text{max}}, \text{nm}(\epsilon)]$:

584 (1,600); 431 (33,100); 387 (5,100). NIR [λ_{max} , nm(ϵ)]:
990 (1,200); 864 (2,800).

62. Bis(bis(t-butylisocyanide)bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5)]- μ -4,4'-methylenebis(3,5-dimethylpyrazolato)-N:N':N'':N''' hexafluorophosphate. $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{-mbpz})\}(\text{PF}_6)_4$.

Compound 62 was prepared by the same procedure used to synthesize 61 by oxidizing 60 (78.5 mg, 0.03 mmol) at +0.25 V. A green solid was obtained upon filtration. The product was recrystallized from CH_2Cl_2 /ether/hexanes and dried in vacuo. Yield 80%.

IR (nujol mull): $\nu_{(\text{CN})}$, $2168\text{ cm}^{-1}(\text{s})$ and $2156\text{ cm}^{-1}(\text{sh})$; $\nu_{(\text{PF}_6^-)}$, $839\text{ cm}^{-1}(\text{s})$ and $557\text{ cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]:
584 (1,970); 432 (35,100); 384sh (4,450). NIR [λ_{max} , nm(ϵ)]:
1008 (920); 865 (1,900).

63. 3,4,5-d₃-pyrazolate analogue of 18. $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-345-d}_3\text{-Pz})]\}(\text{PF}_6)$.

Compound 63 was prepared by the same procedure used to synthesize 18 using 7 (0.3255 g, 0.27 mmol), 1,2,3,4-d₄-pyrazole (39.2 mg, 0.54 mmol) and KOH (0.052 M, 6.18 mL). Yield 90%.

$^{31}\text{P}\{\text{H}\}\text{NMR}$: δ , 24.6 ppm; [$^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}$], 129.4 Hz.
UV-Vis [λ_{max} , nm(ϵ)]: 498 (11,508); 296 (8,275); 265sh (17,050).

64. 3,4,5-d₃-pyrazolate analogue of 24. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-345DPz})]\}(\text{PF}_6)$.

Compound 64 was prepared by the same procedure used to

synthesize 24 using 63 (0.1620 g, 0.13 mmol) and t-BuNC (22.0 mg, 0.26 mmol). Yield 83%.

$^{31}\text{P}\{\text{H}\}$ NMR: δ , 22.7 ppm; [$^1J_{(\text{Rh}-\text{P})} + xJ_{(\text{Rh}-\text{P})}$], 141.6 Hz.

UV-Vis [λ_{max} , nm(ϵ)]: 519 (15,140); 330sh (6,780); 305 (15,000).

65. 3,4,5-d₃-pyrazolate analogue of 34, [Rh₂(μ -dppm)₂(t-BuNC)₂(μ -345-d₃-pz)](PF₆)₂.

Compound 65 was prepared by the same procedure used to synthesize 34 by oxidizing 64 (98.0 mg, 0.07 mmol) at 0.30 V.

UV-Vis [λ_{max} , nm(ϵ)]: 610 (3,170); 430 (29,600).

66. Dicarbonyl- μ -pyrazolato-N:N'bis[μ -methylenebisdiphenylphosphine-P:P']dirhodium(1.5) hexafluorophosphate, [Rh₂(μ -dppm)₂(CO)₂(μ -Pz)](PF₆)₂.

Fifty mL of a CH₂Cl₂ solution of 18 (78.0 mg, 0.06 mmol) containing 0.1 M TBAH was oxidized at +0.83 V via controlled potential electrolysis. The resulting green-brown oxidized solution was stripped to dryness, the residue was dissolved in ca. 100 mL of CH₂Cl₂, and a deep dark green solid precipitate formed upon addition of toluene.

IR (nujol mull): $\nu_{(\text{CO})}$, 2066 cm⁻¹(s) and 2045 cm⁻¹(s); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m). UV-Vis [λ_{max} , nm(ϵ)]: 666 (1,300); 566 (2,700); 519 (3,300); 431 (13,500). NIR [λ_{max} , nm(ϵ)]: 975 (270).

67. Dicarbonyl- μ -4-methylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate, [Rh₂(μ -dppm)₂(CO)₂(μ -4MPz)](PF₆)₂.

Compound 67 was prepared by the same procedure used to

synthesize 66 by oxidizing 20 (78.7 mg, 0.06 mmol) at +0.825 V. A deep dark green solid was isolated.

IR (nujol mull): $\nu_{(\text{CO})}$, 2068 $\text{cm}^{-1}(\text{s})$ and 2040 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]: 665 (840); 565 (1,750); 520 (2,100); 430 (17,000). NIR [λ_{max} , nm(ϵ)]: 982 (200).

68. Dicarbonyl- μ -3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis-(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-35MPz})](\text{PF}_6)_2$.

Compound 68 was prepared by the same procedure used to synthesize 66 by oxidizing 19 (85.7 mg, 0.07 mmol) at +0.85 V. A deep dark green solid was isolated.

IR (nujol mull): $\nu_{(\text{CO})}$, 2055 $\text{cm}^{-1}(\text{s})$ and 2033 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]: 693 (750); 570 (1,500); 519 (2,060); 431 (17,600).

69. Dicarbonyl- μ -4-bromo-3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4B35MPz})](\text{PF}_6)_2$.

Compound 69 was prepared by the same procedure used to synthesize 66 by oxidizing 22 (85.8 mg, 0.06 mmol) at +0.90 V. A deep dark green solid was isolated.

IR (nujol mull): $\nu_{(\text{CO})}$, 2060 $\text{cm}^{-1}(\text{s})$ and 2035 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$. UV-Vis [λ_{max} , nm(ϵ)]: 685 (1,100); 562 (1,600); 491 (3,100); 430 (14,000). NIR [λ_{max} , nm(ϵ)]: 984 (190).

70. Dicarbonyl- μ -3,4,5-tribromopyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(1.5) hexafluorophosphate, [Rh₂(μ -dppm)₂(CO)₂(μ -345BPz)](PF₆)₂.

Compound 70 was prepared by the same procedure used to synthesize 66 by oxidizing 23 (75.4 mg, 0.05 mmol) at +0.95 V. A deep dark green solid was isolated.

IR (nujol mull): $\nu_{(\text{CO})}$, 2075 cm⁻¹(s) and 2049 cm⁻¹(s); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m). UV-Vis [λ_{max} , nm(ϵ)]: 678 (1,300); 575 (2,100); 525 (2,030); 426 (15,600). NIR [λ_{max} , nm(ϵ)]: 985 (280).

71. Bis(t-butylisocyanide)di(η^1 -acetato)- μ -pyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, [Rh₂(μ -dppm)₂(t-BuNC)₂(oAc)₂(μ -Pz)](PF₆).

a. Method 1. A THF solution of 0.29 mL of 1.81 M acetic acid (0.52 mmol) was added dropwise to a THF solution containing 24 (73.1 mg, 0.05 mmol) and TBAH (43.5 mg, 0.11 mmol). After stirring for 1 h, the THF was stripped off and the resulting oil dissolved in CH₂Cl₂. A gold-yellow solid was then obtained upon addition of a 1:1 mixture of ether/hexanes.

b. Method 2. This procedure was the same as Method 1 with the exception being the use of methanol instead of THF as the solvent. The product was recrystallized from CH₂Cl₂/ether/hexanes to obtain a crystalline gold-yellow solid. Yield 84%.

IR (KBr pellet): $\nu_{(\text{CN})}$, 2172 cm⁻¹(s); $\nu_{(\text{PF}_6^-)}$, 839 cm⁻¹(s) and 557 cm⁻¹(m); $\nu_{(\text{C=O})}$, 1601 cm⁻¹(m) and 1574 cm⁻¹(wsh); $\nu_{(\text{C-O})}$, 1358 cm⁻¹(m) and 1314 cm⁻¹(m). ³¹P{H} NMR: δ , 18.3 ppm; [¹J_(Rh-P)

+ $^xJ_{(\text{Rh-P})}$], 95.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 448sh (5,400); 385 (10,450); 312 (15,000); 253sh (27,500). Anal. calcd. for $\text{C}_{67}\text{H}_{71}\text{F}_6\text{N}_4\text{O}_4\text{P}_5\text{Rh}_2 \cdot 0.5 \text{CH}_2\text{Cl}_2$: C, 53.57; H, 4.79; N, 3.70. Found: C, 53.61; H, 4.97; N, 3.65.

72. Bis(t-butylisocyanide)di(η^1 -acetato)- μ -4-methylpyrazolato-N:N'-bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{oAc})_2(\mu\text{-4MPz})](\text{PF}_6)$.

Compound 72 was prepared by the same procedure used to synthesize 71. Methods 1 and 2 were used with 25 (95.8 mg, 0.07 mmol), TBAH (57.9 mg, 0.15 mmol) and 1.81 M acetic acid (0.38 mL, 0.69 mmol) yielding an orange-yellow solid. Yield 77%.

IR(KBr pellet): $\nu_{(\text{CN})}$, 2168 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{C=O})}$, 1599 $\text{cm}^{-1}(\text{m})$ and 1574 $\text{cm}^{-1}(\text{wsh})$; $\nu_{(\text{C-O})}$, 1358 $\text{cm}^{-1}(\text{m})$ and 1314 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 18.45 ppm; [$^1J_{(\text{Rh-P})}$ + $^xJ_{(\text{Rh-P})}$], 95.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 440sh (4,800); 386 (14,000); 315 (21,100); 248sh (38,000).

73. Bis(t-butylisocyanide)di(η^1 -acetato)- μ -3,5-dimethylpyrazolato-N:N'-bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{oAc})_2(\mu\text{-35MPz})](\text{PF}_6)$.

Compound 73 was prepared by the same procedure used to synthesize 71. Method 1, using 26 (97.8 mg, 0.07 mmol), TBAH (62.7 mg, 0.16 mmol) and 1.81 M acetic acid (0.39 mL, 0.71 mmol) gave a gold-yellow solid. Yield 80%.

IR (KBr pellet): $\nu_{(\text{CN})}$, 2168 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{C=O})}$, 1609 $\text{cm}^{-1}(\text{m})$ and 1599 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{C-O})}$, 1358 $\text{cm}^{-1}(\text{m})$ and 1314 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 16.2 ppm; [$^1J_{(\text{Rh-P})}$

+ $^xJ_{(\text{Rh-P})}$], 95.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 470sh (880); 376 (9,050); 309 (12,200); 251sh (18,000).

74. Bis(t-butylisocyanide)di(η^1 -acetato)- μ -4-bromo-3,5-dimethyl-pyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium-(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{oAc})_2(\mu\text{-4B35MPz})](\text{PF}_6)$.

Compound 74 was prepared by the same procedure used to synthesize 71. Method 1, using 28 (83.1 mg, 0.06 mmol), TBAH (42.4 mg, 0.11 mmol) and 1.53 M acetic acid (0.22 mL, 0.34 mmol) afforded an orange-yellow product.

IR (KBr pellet): $\nu_{(\text{CN})}$, 2170 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{C=O})}$, 1603 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{C-O})}$, 1358 $\text{cm}^{-1}(\text{m})$ and 1314 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}\{\text{H}\}$ NMR: δ , 16.1 ppm; [$^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}$], 95.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 480sh (2,300); 387 (28,000); 313 (39,000); 255sh (60,000).

75. Bis(t-butylisocyanide)di(η^1 -acetato)- μ -3,4,5-tribromopyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{oAc})_2(\mu\text{-345BPz})](\text{PF}_6)$.

Compound 75 was prepared by the same procedure used to synthesize 71. Method 1, using 29 (66.2 mg, 0.04 mmol), TBAH (38.3 mg, 0.10 mmol) and 0.89 M acetic acid (0.56 mL, 0.50 mmol) afforded an orange-yellow solid.

$^{31}\text{P}\{\text{H}\}$ NMR: δ , 15.9 ppm; [$^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}$], 92.8 Hz.

76. Bis(t-butylisocyanide)di(η^1 -acetato)- μ -1,2,4-triazolato-N:N'bis-[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{oAc})_2(\mu\text{-Tz})](\text{PF}_6)$.

Compound 76 was prepared by the same procedure used to synthesize 71. Method 1, using 27 (74.0 mg, 0.05 mmol), TBAH (43.6 mg, 0.11 mmol) and 0.90 M acetic acid (0.60 mL, 0.54 mmol) afforded an orange-yellow solid.

IR (KBr pellet): $\nu_{(\text{CN})}$, 2176 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$; $\nu_{(\text{C=O})}$, 1601 $\text{cm}^{-1}(\text{m})$ and 1574 $\text{cm}^{-1}(\text{wsh})$; $\nu_{(\text{C-O})}$, 1358 $\text{cm}^{-1}(\text{m})$ and 1312 $\text{cm}^{-1}(\text{m})$. $^{31}\text{P}(\text{H})$ NMR: δ , 17.2 ppm; [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$], 95.2 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 450sh (7,200); 388 (18,500); 322 (25,900); 259sh (50,000).

77. Bis(t-butylisocyanide)di(η^1 -nitrate)- μ -pyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{NO}_3)_2(\mu\text{-Pz})](\text{PF}_6)$.

A THF solution containing 0.09 mL of 1.06 M HNO_3 (0.095 mmol) was added dropwise to a THF solution containing 24 (63.3 mg, 0.05 mmol) and TBAH (38.2mg, 0.10 mmol). After stirring for ca 2 h, the THF solution was stripped off via rotary evaporator. The resulting residue was dissolved in CH_2Cl_2 and an orange solid was obtained upon addition of a 1:1 mixture of ether/hexanes. The product was recrystallized from CH_2Cl_2 /ether/hexanes to obtain a crystalline orange solid.

IR (KBr pellet): $\nu_{(\text{CN})}$, 2182 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$; $\nu_{\text{a}(\text{NO}_2)}$, 1466 $\text{cm}^{-1}(\text{wsh})$; $\nu_{\text{s}(\text{NO}_2)}$, 1258 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{NO})}$, 1003 $\text{cm}^{-1}(\text{w})$ and 1007 $\text{cm}^{-1}(\text{w})$. $^{31}\text{P}(\text{H})$ NMR: δ , 16.2 ppm;

$[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, 92.8 Hz. UV-Vis $[\lambda_{\text{max}}, \text{nm}(\epsilon)]$: 480 (1,500); 350 (17,200); 268 (29,000).

78. Bis(t-butylisocyanide)di(η^1 -nitrate- μ -4-methylpyrazolato-N:N'-bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{NO}_3)_2(\mu\text{-4MPz})](\text{PF}_6)$.

Compound 78 was prepared by the same procedure used to synthesize 77 by using 25 (78.6 mg, 0.06 mmol), TBAH (55.1 mg, 0.14 mmol) and 1.06 M HNO_3 (0.11 mL, 0.12 mmol) to obtain an orange solid.

IR (KBr pellet): $\nu_{(\text{CN})}$, 2180 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$; $\nu_{\text{a}(\text{NO}_2)}$, 1466 $\text{cm}^{-1}(\text{w})$; $\nu_{\text{s}(\text{NO}_2)}$, 1258 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{NO})}$, 1000 $\text{cm}^{-1}(\text{w})$ and 991 $\text{cm}^{-1}(\text{w})$. $^{31}\text{P}\{\text{H}\}$ NMR: δ , 16.2 ppm; $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, 92.8 Hz. UV-Vis $[\lambda_{\text{max}}, \text{nm}(\epsilon)]$: 470sh (2,200); 350 (22,000); 266 (40,200). Anal. calcd. for $\text{C}_{64}\text{H}_{67}\text{F}_6\text{N}_6\text{O}_6\text{P}_5\text{Rh}_2 \cdot \text{CH}_2\text{Cl}_2$: C, 49.54; H, 4.41; N, 5.33. Found: C, 48.75; H, 5.09; N, 5.22.

79. Bis(t-butylisocyanide)di(η^1 -nitrate)- μ -3,5-dimethylpyrazolato-N:N'-bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II) hexafluorophosphate. $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{NO}_3)_2(\mu\text{-35MPz})](\text{PF}_6)$.

Compound 79 was prepared by the same procedure used to synthesize 77 by using 26 (75.5 mg, 0.05 mmol), TBAH (48.4 mg, 0.12 mmol) and 1.06 M HNO_3 (0.10 mL, 0.11 mmol) to obtain an orange solid. Yield 95%.

IR (KBr pellet): $\nu_{(\text{CN})}$, 2178 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$; $\nu_{\text{a}(\text{NO}_2)}$, 1462 $\text{cm}^{-1}(\text{w})$; $\nu_{\text{s}(\text{NO}_2)}$, 1258 $\text{cm}^{-1}(\text{w})$; $\nu_{(\text{NO})}$, 1001 $\text{cm}^{-1}(\text{w})$ and 1011 $\text{cm}^{-1}(\text{w})$. $^{31}\text{P}\{\text{H}\}$ NMR: δ , 14.3 ppm;

$[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, 92.8 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 480 (1,400); 361 (26,000); 271 (38,000).

80. Bis(t-butylisocyanide)di(η^1 -nitrate)- μ -4-bromo-3,5-dimethylpyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II)hexafluorophosphate, $\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{NO}_3)_2(\mu\text{-4B35MPz})](\text{PF}_6)$.

Compound 80 was prepared by the same procedure used to synthesize 77 by using 28 (80.9 mg, 0.05 mmol), TBAH (46.0 mg, 0.12 mmol) and 0.37 M HNO_3 (0.42 mL, 0.15 mmol) to obtain an orange solid.

IR (KBr pellet): $\nu_{(\text{CN})}$, 2180 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$; $\nu_{\text{a}(\text{NO}_2)}$, 1462 $\text{cm}^{-1}(\text{w})$; $\nu_{\text{s}(\text{NO}_2)}$, 1258 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{NO})}$, 1001 $\text{cm}^{-1}(\text{w})$. $^{31}\text{P}(\text{H})$ NMR: δ , 14.2 ppm; $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, 92.8 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 466 (700); 363 (13,000); 272 (19,000).

81. Bis(t-butylisocyanide)di(η^1 -nitrate)- μ -3,4,5-tribromopyrazolato-N:N'bis[μ -methylenebis(diphenylphosphine)-P:P']dirhodium(II)hexafluorophosphate, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{NO}_3)_2(\mu\text{-345BPz})](\text{PF}_6)$.

Compound 81 was prepared by the same procedure used to synthesize 77 by using 29 (83.2 mg, 0.06 mmol), TBAH (53.3 mg, 0.14 mmol) and 1.06 M HNO_3 (0.11 mL, 0.12 mmol) to obtain an orange solid.

IR (KBr pellet): $\nu_{(\text{CN})}$, 2180 $\text{cm}^{-1}(\text{s})$; $\nu_{(\text{PF}_6^-)}$, 839 $\text{cm}^{-1}(\text{s})$ and 557 $\text{cm}^{-1}(\text{m})$; $\nu_{\text{a}(\text{NO}_2)}$, 1464 $\text{cm}^{-1}(\text{w})$; $\nu_{\text{s}(\text{NO}_2)}$, 1256 $\text{cm}^{-1}(\text{w})$; $\nu_{(\text{NO})}$, 991 $\text{cm}^{-1}(\text{w})$. $^{31}\text{P}(\text{H})$ NMR: δ , 14.2 ppm; $[^1J_{(\text{Rh-P})} +$

$^xJ_{(\text{Rh-P})}$], 92.8 Hz. UV-Vis [λ_{max} , nm(ϵ)]: 470sh (1,450); 366 (22,000); 278 (34,000).

I. Compound Identification

Table I lists by number all compounds appearing in Chapters III-VII. An explanation of abbreviations used appears at the end of the table.

TABLE I

COMPOUND IDENTIFICATION

Compound number	Compound
1	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})](\text{PF}_6)$
2	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2]$
3	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-CO})(\mu\text{-Cl})](\text{PF}_6)$
4	$[\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-CO})\text{Cl}_2(\mu\text{-Cl})](\text{PF}_6)$
5	$[\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-CO})\text{Cl}_2]$
6	$[\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-}^{13}\text{CO})\text{Cl}_2]$
7	$[\text{Rh}_2(\mu\text{-dppp})_2\text{COCl}_3(\mu\text{-NO}_3)]$
8	$[\text{Rh}_2(\mu\text{-dppp})_2^{13}\text{COCl}_3(\mu\text{-NO}_3)]$
9	$[\text{Rh}_2(\mu\text{-dppp})\text{CO}(\mu\text{-Cl})\text{Cl}_3]$
10	$[\text{Rh}_2(\mu\text{-dppp})_2^{13}\text{CO}(\mu\text{-Cl})\text{Cl}_3]$
11	$[\text{Rh}_2(\mu\text{-dppp})_2(\text{CO})_2\text{Cl}_4]$
12	$[\text{Rh}_2(\mu\text{-dppp})_2(\underline{\text{t}}\text{-BuNC})_2\text{Cl}_4]$
13	$[\text{Rh}_2(\mu\text{-dppp})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-Cl})\text{Cl}_2](\text{PF}_6)$
14	$[\text{Rh}_2(\mu\text{-dppm})_2\text{CO}(\mu\text{-Cl})\text{Cl}_3]$
15	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}_2](\text{PF}_6)$
16	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_4]$
17	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-Cl})\text{Cl}_2](\text{PF}_6)$
18	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Pz})](\text{PF}_6)$
19	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-35MPz})](\text{PF}_6)$
20	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4MPz})](\text{PF}_6)$

TABLE I (Continued)

Compound number	Compound
21	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Tz})](\text{PF}_6)$
22	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4B35MPz})](\text{PF}_6)$
23	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-345BPz})](\text{PF}_6)$
24	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-Pz})](\text{PF}_6)$
25	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)$
26	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)$
27	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-Tz})](\text{PF}_6)$
28	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4B35MPz})](\text{PF}_6)$
29	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345BPz})](\text{PF}_6)$
30	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})(\underline{\text{t}}\text{-BuNC})(\mu\text{-Pz})](\text{PF}_6)$
31	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})(\underline{\text{t}}\text{-BuNC})(\mu\text{-4MPz})](\text{PF}_6)$
32	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})(\underline{\text{t}}\text{-BuNC})(\mu\text{-35MPz})](\text{PF}_6)$
33	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})(\underline{\text{t}}\text{-BuNC})(\mu\text{-Tz})](\text{PF}_6)$
34	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-Pz})](\text{PF}_6)_2$
35	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)_2$
36	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$
37	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-4B35MPz})](\text{PF}_6)_2$
38	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345BPz})](\text{PF}_6)_2$
39	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-Tz})](\text{PF}_6)_2$
40	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)$
41	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Cl}_2(\mu\text{-4MPz})](\text{PF}_6)$
42	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Cl}_2(\mu\text{-35DMPz})](\text{PF}_6)$

TABLE I (Continued)

Compound number	Compound
43	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Cl}_2(\mu\text{-Tz})](\text{PF}_6)$
44	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Br}_2(\mu\text{-Pz})](\text{PF}_6)$
45	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Br}_2(\mu\text{-4MPz})](\text{PF}_6)$
46	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Br}_2(\mu\text{-35MPz})](\text{PF}_6)$
47	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Br}_2(\mu\text{-Tz})](\text{PF}_6)$
48	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{Br}_2(\mu\text{-345BPz})](\text{PF}_6)$
49	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{I}_2(\mu\text{-Pz})](\text{PF}_6)$
50	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{I}_2(\mu\text{-4MPz})](\text{PF}_6)$
51	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{I}_2(\mu\text{-35MPz})](\text{PF}_6)$
52	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2\text{I}_2(\mu\text{-Tz})](\text{PF}_6)$
53	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{SCN})_2(\mu\text{-Pz})](\text{PF}_6)$
54	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{SCN})_2(\mu\text{-4MPz})](\text{PF}_6)$
55	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{SCN})_2(\mu\text{-35MPz})](\text{PF}_6)$
56	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2((\text{SCN})_2(\mu\text{-Tz}))](\text{PF}_6)$
57	$\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2]_2(\mu\text{-bPz})\}(\text{PF}_6)_2$
58	$\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2]_2(\mu\text{-mbPz})\}(\text{PF}_6)_2$
59	$\{[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2]_2(\mu\text{-bPz})\}(\text{PF}_6)_2$
60	$\{[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2]_2(\mu\text{-mbPz})\}(\text{PF}_6)_2$
61	$\{[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2]_2(\mu\text{-bPz})\}(\text{PF}_6)_4$
62	$\{[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2]_2(\mu\text{-mbPz})\}(\text{PF}_6)_4$
63	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-345d}_3\text{Pz})](\text{PF}_6)$
64	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345d}_3\text{Pz})](\text{PF}_6)$

TABLE I (Continued)

Compound number	Compound
65	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-345d}_3\text{Pz})](\text{PF}_6)_2$
66	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Pz})](\text{PF}_6)_2$
67	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4MPz})](\text{PF}_6)_2$
68	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-35MPz})](\text{PF}_6)_2$
69	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4B35MPz})](\text{PF}_6)_2$
70	$[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-345BPz})](\text{PF}_6)_2$
71	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{oAc})_2(\mu\text{-Pz})](\text{PF}_6)$
72	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{oAc})_2(\mu\text{-4MPz})](\text{PF}_6)$
73	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{oAc})_2(\mu\text{-35MPz})](\text{PF}_6)$
74	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{oAc})_2(\mu\text{-4B35MPz})](\text{PF}_6)$
75	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{oAc})_2(\mu\text{-345BPz})](\text{PF}_6)$
76	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{oAc})_2(\mu\text{-Tz})](\text{PF}_6)$
77	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{NO}_3)_2(\mu\text{-Pz})](\text{PF}_6)$
78	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{NO}_3)_2(\mu\text{-4MPz})](\text{PF}_6)$
79	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{NO}_3)_2(\mu\text{-35MPz})](\text{PF}_6)$
80	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{NO}_3)_2(\mu\text{-4B35MPz})](\text{PF}_6)$
81	$[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\text{NO}_3)_2(\mu\text{-345BPz})](\text{PF}_6)$
82	$[\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})]$

Abbreviations used in table:

dppm - Bis(diphenylphosphino)methane

dppp - 2-(diphenylphosphino)pyridine

Abbreviations used in table (Continued):

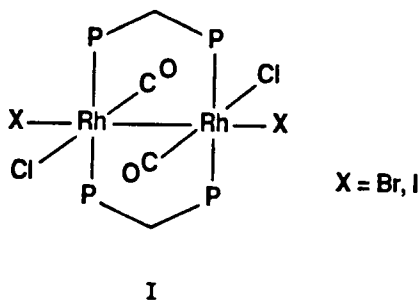
t-BuNC	- t-butylisocyanide
Pz	- pyrazolate
4MPz	- 4-methylpyrazolate
35MPz	- 3,5-dimethylpyrazolate
4B35MPz	- 4-bromo-3,5-dimethylpyrazolate
345BPz	- 3,4,5-tribromopyrazolate
Tz	- triazolate
bPz	- 3,5,3',5'-tetramethyl-4,4'-bipyrazolate
mbPz	- 4,4'-methylenebis(3,5-dimethylpyrazolate)

CHAPTER III

ELECTROCHEMISTRY AND REACTIVITY OF BINUCLEAR RHODIUM COMPLEXES CONTAINING CARBON MONOXIDE AND ISOCYANIDE LIGANDS WITH DPPM AS THE BRIDGING LIGAND

Investigation of the chemical behavior of dinuclear rhodium complexes containing transoid dppm ligands has been for the most part restricted to dinuclear Rh(I) complexes. Increasing interest in these complexes has arisen from their potential application as homogeneous catalysts. Since trans-Rh₂(μ-dppm)₂(CO)₂Cl₂, 2, was first reported, it has served as a precursor to numerous other dinuclear rhodium complexes. In some cases oxidative addition of various reagents to 2 or some of its Rh(I) derivatives has clearly produced rhodium dimers with a formal oxidation state of two.^{2,7,31,82} In other cases, such as with cis-dimetallated olefins,^{13,28,29,55,83} there is some uncertainty as to the formal oxidation state of the metal atoms.

The oxidative addition of bromine or iodine to 2^{2,7} has led to Rh(II) complexes with Structure I.

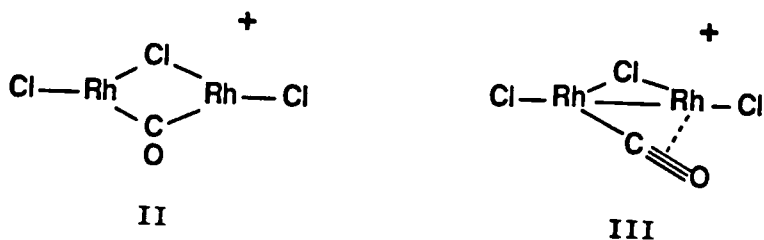


However, the chloro analogue to I has not been reported, and attempts to prepare this derivative have led to a mixture of products that has thus far defied separation and characterization.

Previous studies by D. Womack and P. Enlow^{18,19} involving electrochemistry of dinuclear Rh(I) complexes in the presence of coordinating species suggest that electrochemical oxidation of complexes such as 2 in the presence of halide ions might generate $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_4$ with Structure I. Taking this approach, P. Tinsley⁷⁹ investigated the electrochemical behavior of 2 in a CH_2Cl_2 solution containing 0.1 M TBAH and excess TBAC. His work demonstrated that a yellow solution of 2 in the presence of excess chloride ions exhibits an irreversible anodic wave at +0.40 V, with the corresponding cathodic waves at -0.55 and -0.70 V on the cyclic voltammetric time scale. He determined that controlled-potential coulometry at +0.60 V results in a two electron oxidation and that an IR spectrum of the residue after removal of the solvent exhibits a CO stretching frequency at 2024 cm^{-1} which is assigned to a terminal CO. Tinsley further demonstrated that treatment of the oxidized solution with methanol to remove the tetra-n-butylammonium salts results in the isolation of a green solid. After recrystallization from CH_2Cl_2 , the product exhibits an IR band at 1794 cm^{-1} which is consistent with the presence of a bridging carbonyl ligand. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of this product exhibits the typical AA'A''A'''XX' pattern observed for symmetrical rhodium dimers containing two trans bridging dppm ligands. The spectroscopic and analytical data, which reveal the presence of

three chloride ions, are consistent with the formulation of the green solid as $[\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-CO})](\text{PF}_6)$, 4.

Two different structural formulations of 4 are possible. One has the bridging carbonyl symmetrically bound to the two rhodium atoms. This formulation requires that CO be a two-electron donor, resulting in no formal Rh-Rh bond (ketonic carbonyl) as indicated by Structure II. The other possible formulation is one in which the CO acts as a four-electron donor, and thus is unsymmetrically bound to the two rhodium atoms as shown by Structure III.

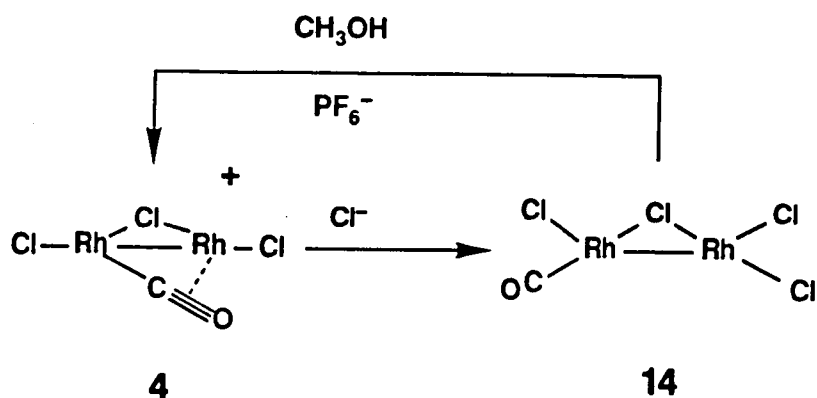


Structure III requires the formation of a metal-metal bond. It has been suggested by M. Cowie⁸³ that complexes with structures such as II are likely to be unstable due to non-bonded contacts of the bridging CO and the bridging ligand opposite the CO created by the large metal-metal separation.

The general trend for the values of the coupling constant, $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, in dppm dirhodium complexes is that for complexes with a Rh-Rh bond the values of the coupling constant are usually in the range of 90-115 Hz, and those for complexes with no Rh-Rh bond are in the range of 125-140 Hz.^{10,14,15,83} The observed value of 97.7 Hz for 4 is in the range of values generally observed for dppm-bridged dirhodium complexes that contain a Rh-Rh bond.

Structure III, however, is not consistent with the symmetrical AA'A''A'''XX' $^{31}\text{P(H)}$ NMR pattern unless the complex is fluxional, thus leading to equivalent time-averaged environments for the four phosphorus atoms. The $^{31}\text{P(H)}$ NMR spectrum has been measured over the temperature range -90 to $+25$ $^{\circ}\text{C}$. There was no observable change in the spectrum over this range; therefore, if interconversion is occurring, it is rapid at -90 $^{\circ}\text{C}$.

It has been postulated by C. Janke⁸¹ that in the conversion of 2 to 4, $\text{Rh}_2(\mu\text{-dppm})_2\text{CO}(\mu\text{-Cl})\text{Cl}_3$, 14, is formed as the initial oxidation product and is then converted to 4 during isolation procedures. This behavior suggests that at least one of the chloro ligands on 14 is labile enough such that the ionizing power of methanol facilitates its removal during attempts to isolate 14 from a solution containing a non-coordinating anion such as PF_6^- . Janke also demonstrated that treatment of 4 with excess chloride generates the initial oxidation product 14.



Further evidence that 14 is the initial oxidation product is derived from the $^{31}\text{P(H)}$ NMR and UV-Vis data of the oxidized solution

when the oxidation of 2 is performed in a CH_2Cl_2 solution containing 0.1 M TBAB and excess TBAC. The $^{31}\text{P}(\text{H})$ NMR and UV-Vis data obtained directly from the oxidized solution are identical to that obtained from the reaction of 4 with excess chloride.

Compound 14 can also be prepared from the oxidation of 2 in a CH_2Cl_2 solution containing TBAN and excess TBAC. The cyclic voltammogram of 2 in TBAN in the limits -1.5 to +1.0 V exhibits an irreversible cathodic wave at -1.35 V, with the corresponding anodic wave at -0.07 V when the potential is initially scanned in the negative direction. Also present is a broad irreversible anodic wave centered at +0.65 V with two corresponding cathodic waves at -0.03 and -0.55 V (Figure 4A). When an excess of chloride ions are added to the solution, the cyclic voltammogram of 2 reveals an irreversible oxidation wave at +0.481 V with the corresponding reduction wave at -0.762 V (Figure 4B). Controlled-potential coulometry at +0.75 V indicates that 2 undergoes a two-electron oxidation in the presence of chloride.

The HOMO of face-to-face dppm bridged dirhodium (I) compounds such as 2 has been described as a doubly occupied σ^* (d_z^2) molecular orbital.⁶ Therefore, the oxidation of 2 represented by the anodic wave at +0.57 V leads to the removal of these electrons resulting in a transformation from Rh(I)-Rh(I) to a Rh(II)-Rh(II) species. The electrolysis product exhibits an irreversible reduction wave at -0.863 V with a corresponding anodic wave at +0.328 V (Figure 4C). Washing a reduced volume of the oxidized solution with water to remove the tetra-*n*-butylammonium salts results in the isolation of a

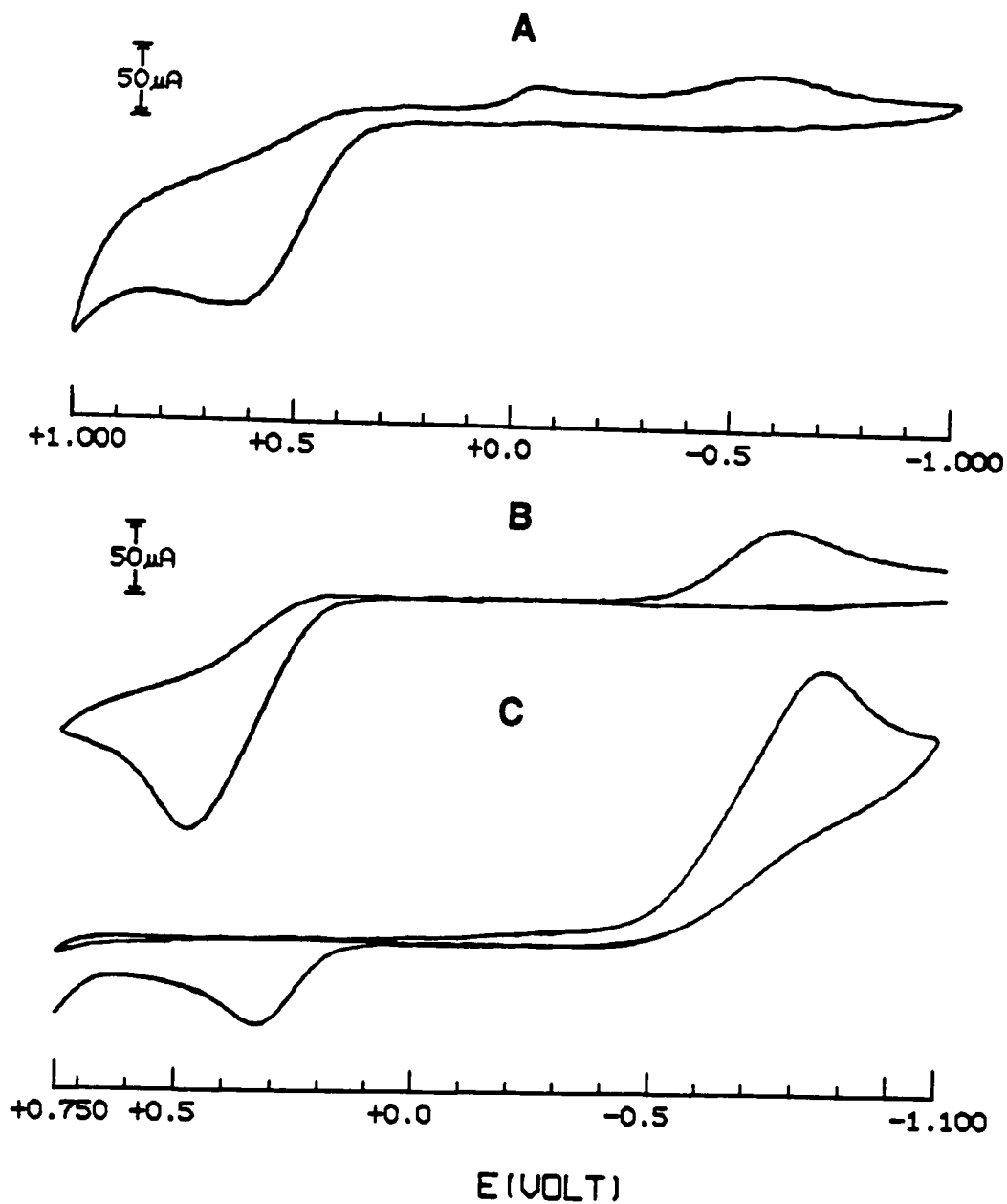


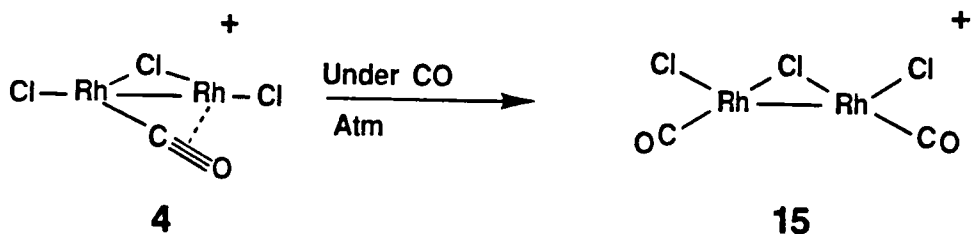
Figure 4. Cyclic voltammograms of $1.2 \times 10^{-4} \text{ M Rh}_2(\mu\text{-dppm})_2\text{-Cl}_2(\text{CO})_2$, **2**, (A) in $0.1 \text{ M TBAN/CH}_2\text{Cl}_2$, (B) before oxidation in the presence of $6.0 \times 10^{-4} \text{ M TBAC}$, and (C) after oxidation in $\text{TBAN/TBAC/CH}_2\text{Cl}_2$

brown solid upon addition of ether. The spectroscopic data of the brown solid are identical to that of 14, thus the electrochemical oxidation of 2 in excess chloride is formulated as 14.

Although many dirhodium carbonyl complexes containing two bridging dppm ligands in a trans disposition are fluxional,^{24,82} the ³¹P{H} NMR spectra of 14 remains essentially unchanged over the temperature range -85 to +35 °C. This indicates that exchange is either not occurring or is still rapid at -85 °C.

A. Reaction of $[\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-CO})](\text{PF}_6)$
with Carbon Monoxide

When CO is passed over an open acetone solution of 4, the solution turns orange instantaneously. Upon addition of 1:1 ether/hexanes solution an orange product precipitates. The IR spectrum reveals the presence of a PF_6^- counter ion and terminal CO ligands with stretching frequencies of 2058(s) and 2025(sh) cm^{-1} . The analytical data indicate the presence of three chloride ligands and one mole of dichloromethane. These data are consistent with the formulation of the product as $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2(\mu\text{Cl})](\text{PF}_6) \cdot \text{CH}_2\text{Cl}_2$, 15, with the structure of the cation shown below.



The bridging chloride is postulated on the basis of the electron count of 18 for each rhodium, and the symmetrical AA'A''A'''XX' $^{31}\text{P(H)}$ NMR pattern. The NMR spectrum exhibits a chemical shift of 11.3 ppm and a $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 75.7 Hz. Treating a solution of 15 with dinitrogen does not result in the degradation of 15, but attempts to grow crystals of 15 by slow diffusion of ether over several days results in the formation of 4.

When a solution of 4 or 15 is bubbled with CO for several minutes or is allowed to stand under a CO atmosphere overnight, the solution turns orange-yellow. The $^{31}\text{P(H)}$ NMR and IR data of the product isolated from this solution are identical to that of a freshly prepared sample of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})](\text{PF}_6)$, 1. On the other hand, if a solution of 4 or 15 is kept under an atmosphere of CO and the product is not isolated, the $^{31}\text{P(H)}$ NMR spectrum of the solution indicates that the complex present is $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-CO})](\text{PF}_6)$. These observations are consistent with previous results that show that $[[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-CO})](\text{PF}_6)]$ is formed when a solution of 1 is saturated with carbon monoxide.²³

The conversion of 4 or 15 to 1 involves the reduction of a Rh(II) dimer to a Rh(I) dimer. Although there have not been any CO oxidation products identified, it has been demonstrated, using a chloride-ion selective electrode, that a stoichiometric amount of chloride ion is produced as 4 or 15 is converted to 1. These

results suggest that the conversion is not a simple reductive elimination of elemental chlorine but a reduction by CO accompanied by the loss of a chloride ion.

The cyclic voltammogram of 4 in CH₂Cl₂/TBAH reveals two irreversible cathodic waves at -0.21 and -0.79 V with an associated anodic wave at +0.82 V (Figure 5A). Controlled-potential coulometry at -0.90 V indicates a two-electron transfer process per rhodium dimer. The cyclic voltammogram of the reduced solution reveals an irreversible oxidation wave at +0.76 V with the corresponding reduction waves at -0.16, -0.41 and -0.73 V (Figure 5B). The reduction product, isolated from methanol, contains a bridging carbonyl ligand with an IR stretching frequency of 1745 cm⁻¹. The AA'A''A'''XX' ³¹P(H) NMR pattern with a [¹J_(Rh-P) + ^xJ_(Rh-P)] value of 117.2 Hz suggests a symmetrical species with a Rh-Rh bond. The ³¹P(H) NMR spectrum also indicates the absence of PF₆⁻ counter ions. These data are consistent with those reported for Rh₂(μ-dppm)₂Cl₂(μ-CO),¹⁰ and thus the electrochemical reduction product of 4 is formulated as Rh₂(μ-dppm)₂Cl₂(μ-CO), 82.

The difference between the electrochemical reduction product of 4 and the CO reduction product of 4 is the presence of excess CO during the CO reduction process. For CO reduction, excess CO is available to coordinate to the rhodium atoms and stabilize their low oxidation state. In the electrochemical reduction there is no CO available, thus the neutral species, 82, is the isolated product. The reactions describing the above results are shown on page 96.

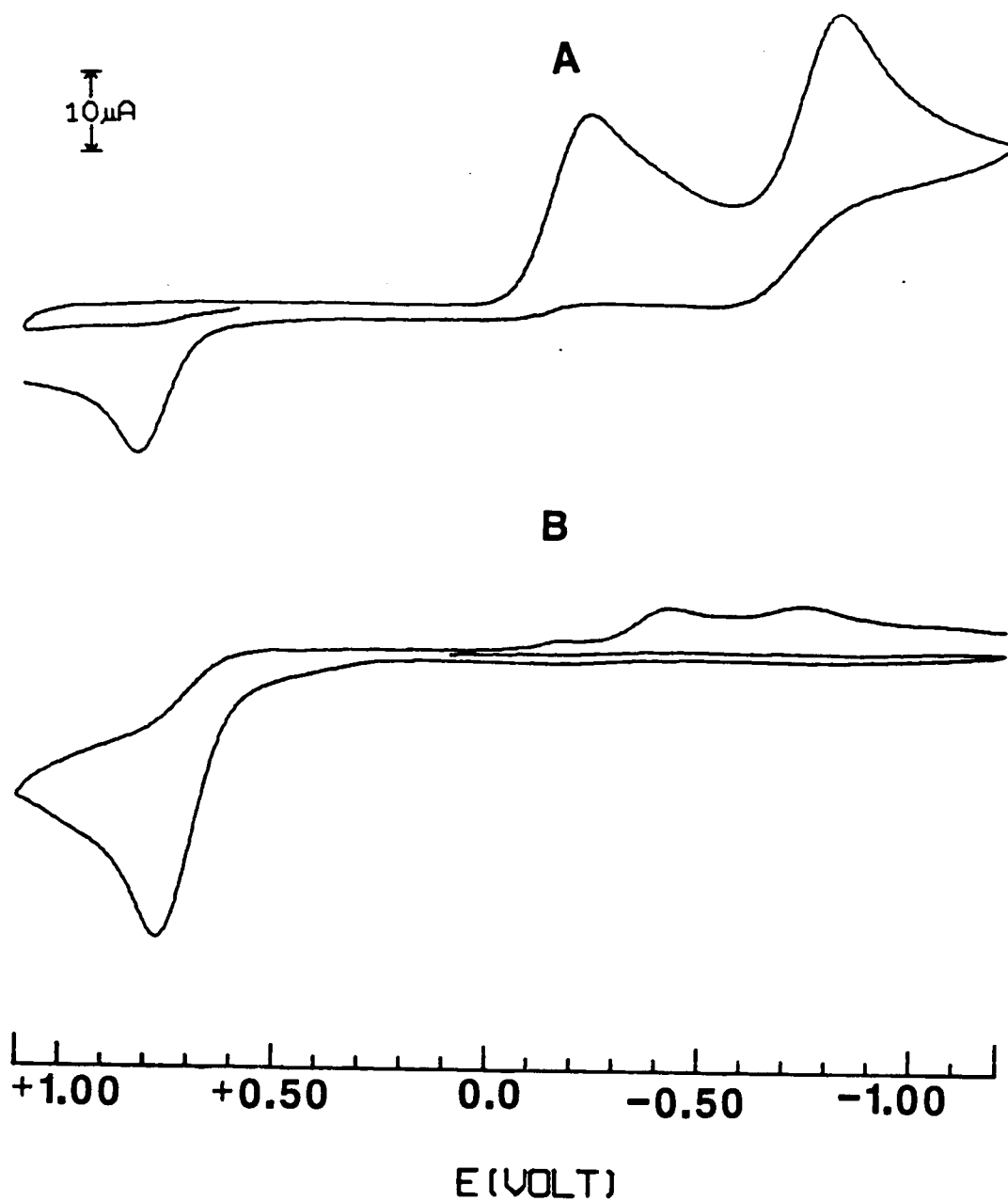
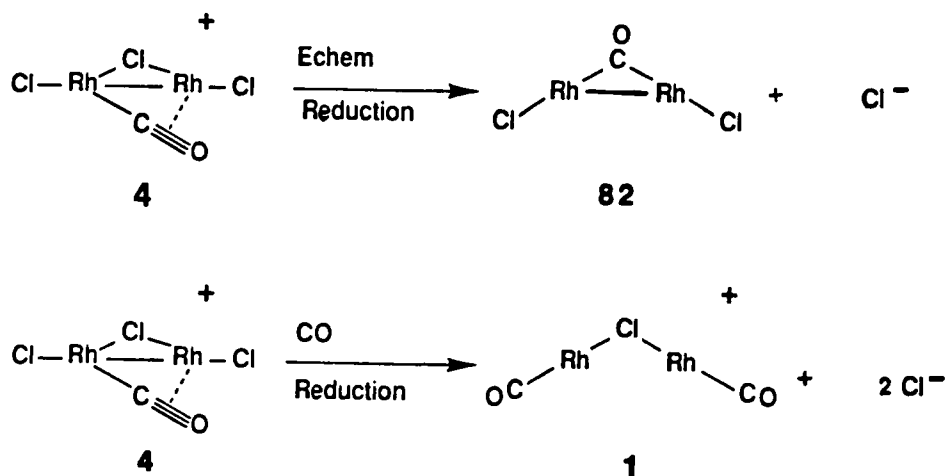


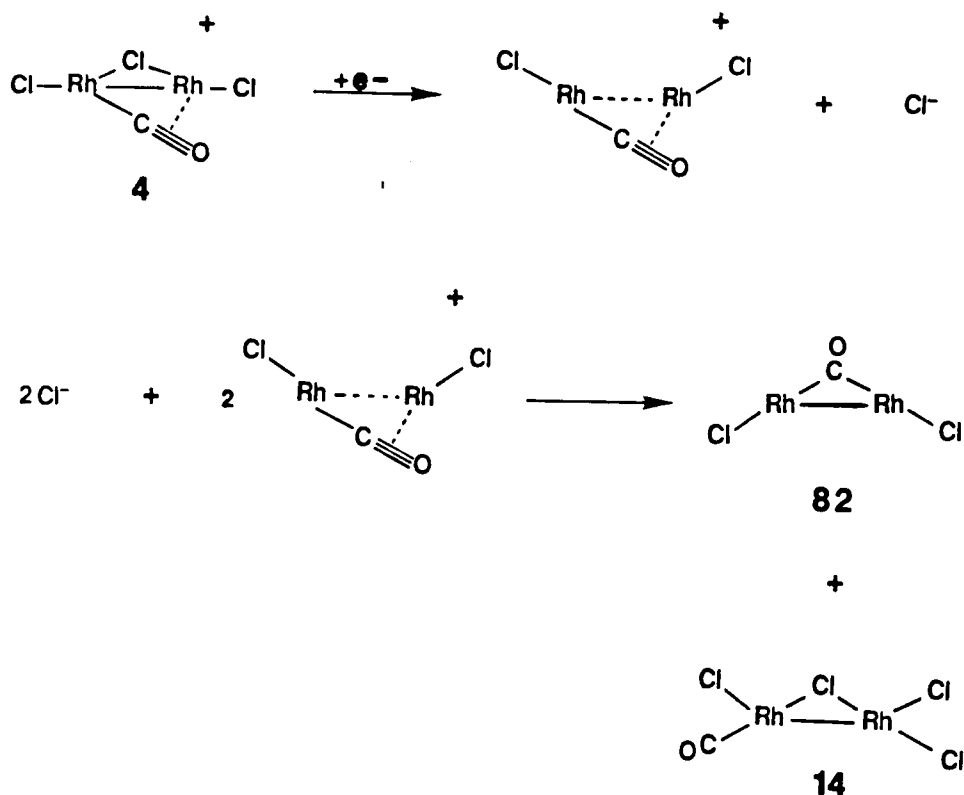
Figure 5. Cyclic voltammograms of 5.7×10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-CO})\text{Cl}_2(\mu\text{-Cl})](\text{PF}_6)_2$, **4**, in 0.1 M TBAH/ CH_2Cl_2 (A) before reduction and (B) after reduction.



Bulk electrolysis of 4 at -0.30 V between the two cathodic waves results in a one-electron transfer per rhodium dimer. The IR spectrum of the product isolated from methanol reveals two strong bridging carbonyl bands at 1745 and 1794 cm^{-1} . These carbonyl stretching frequencies at 1745 and 1794 cm^{-1} indicate the formation of a dinuclear Rh(I) and a dinuclear Rh(II) species instead of a mixed-valence dimer.

When the one-electron reduction of 4 is performed in a CH_2Cl_2 solution containing 0.1 M TBAB, the $^{31}\text{P}(\text{H})$ NMR spectrum of the reduced solution reveals the presence of 14 and 82. The formation of 14 and 82 from a one-electron reduction is a result of an EC mechanism. The one-electron reduction accompanied by the loss of a chloride ion first generates a mixed-valence species. The free chloride ion then induces a disproportionation reaction resulting in the formation of a Rh(I) dimer, 82, and a Rh(II) dimer, 14. The EC reduction mechanism is summarized in Scheme I.

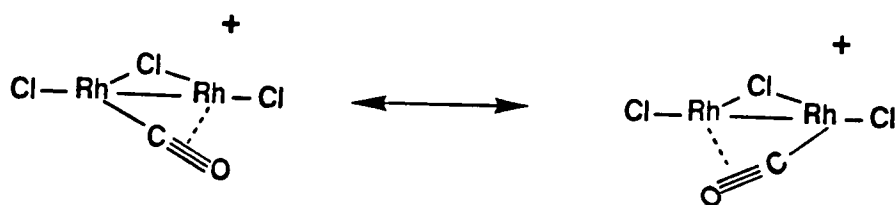
Scheme I.



The structure of the transient mixed-valence species shown in Scheme I is postulated as $[\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_2(\mu\text{-CO})](\text{PF}_6)$ with an unsymmetrical bridging carbonyl ligand.

The removal of CH_2Cl_2 from the reduced solution of **4** and subsequent dissolution of the residue in an acetone-methanol solution results in the formation of **4** and **82**. The conversion of **14** to **4** has been previously shown to occur when **14** is treated with methanol.⁸¹ The formation of **4** and **82** is also consistent with the presence of IR bands at 1794 and 1745 cm^{-1} observed for the product isolated after the one-electron reduction of **4** in a $\text{TBAH}/\text{CH}_2\text{Cl}_2$ solution.

Variable-temperature $^{31}\text{P}(\text{H})$ NMR spectra of the solution containing TBAB, methanol, acetone, and one-half equivalent chloride ion are shown in Figure 6. At +25 and +50 $^{\circ}\text{C}$, the phosphorus resonance due to 4 is broad which suggests a fluxional process. Lowering the temperature to -50 $^{\circ}\text{C}$ results in a sharpening of the phosphorus resonance lines of 4. The observed fluxional process in the above medium is supporting evidence that 4 contains an unsymmetrical bridging carbonyl ligand. The fluxional behavior shown in Figure 6 results from the exchange of the carbonyl's σ/π interaction between the two rhodium atoms as shown below.



B. Reaction of $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_3(\mu\text{-Cl})\text{CO}$
with Carbon Monoxide

When CO is bubbled through a CH_2Cl_2 solution of 14, the solution turns orange. Upon addition of 1:1 ether/hexanes, a dark orange product is obtained. The $^{31}\text{P}(\text{H})$ NMR spectrum of the product exhibits the AA'A''A'''XX' pattern with a $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 87.9 Hz. These data indicate that the complex is a symmetrical Rh(II) dimer containing four chemically equivalent phosphorus atoms, and suggest that it contains a metal-metal bond. The solid state IR spectrum reveals a band at 2041 cm^{-1} which indicates the presence of terminal carbonyl ligands. The conversion is

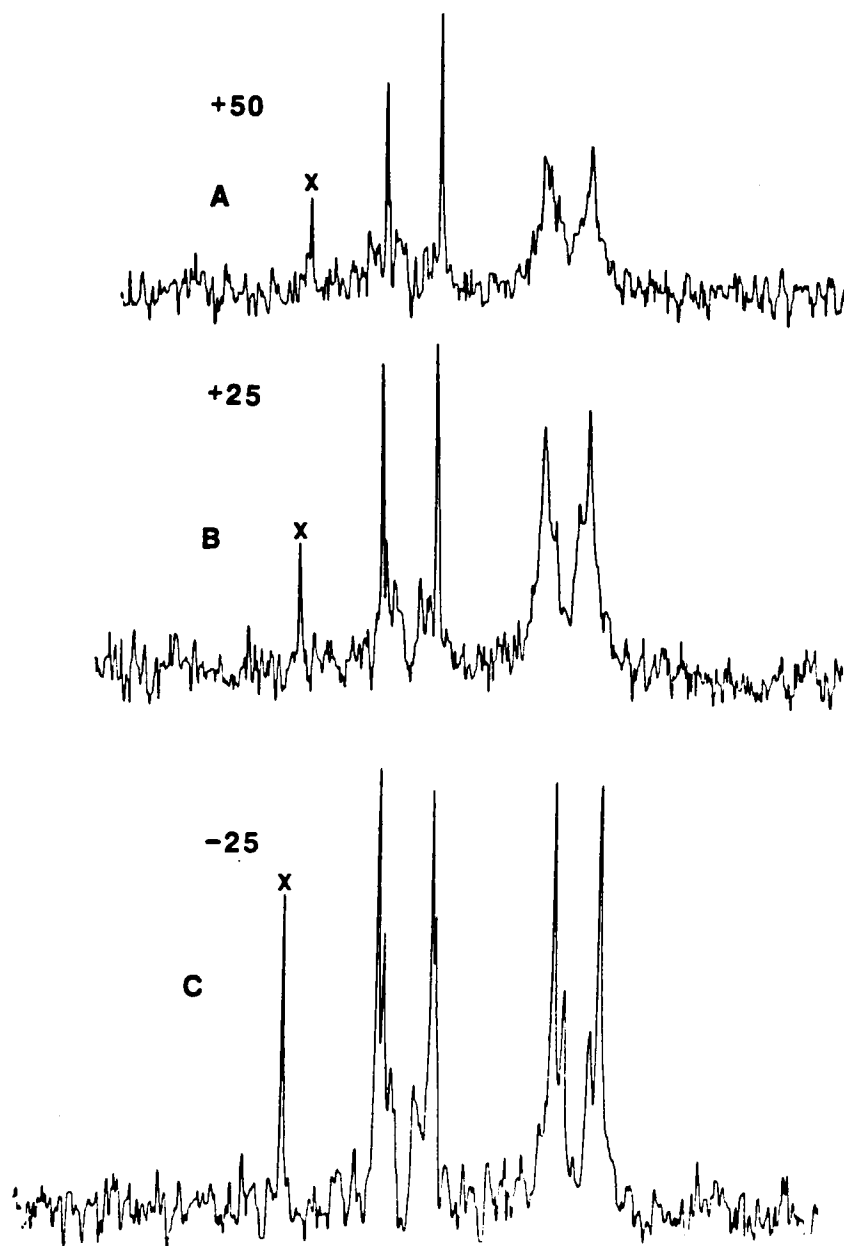
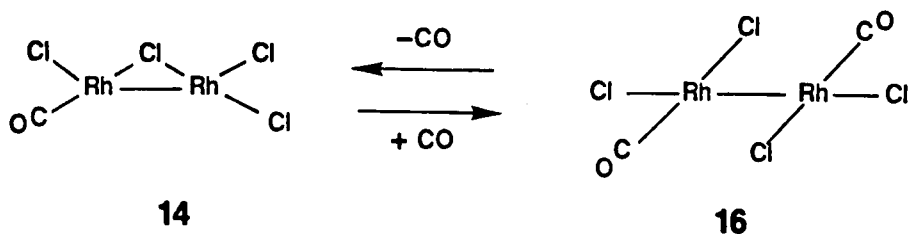


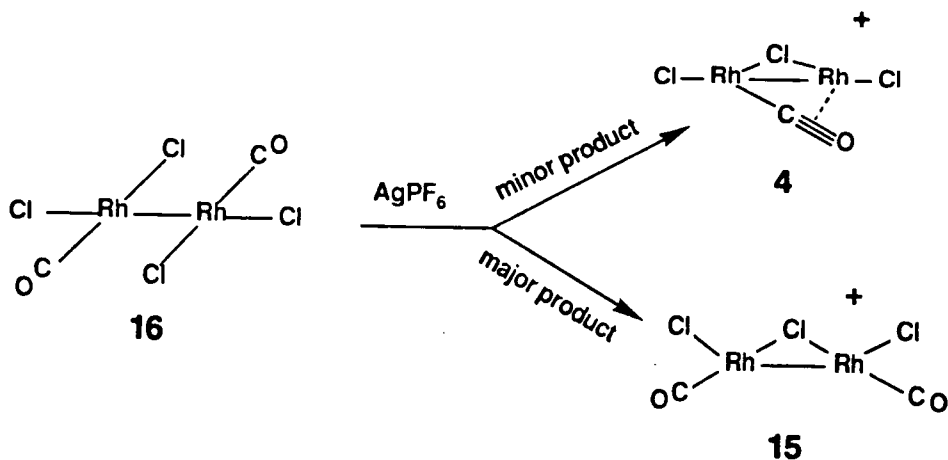
Figure 6. Variable-temperature $^{31}\text{P}(\text{H})$ NMR spectra of the one-electron reduced $[\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-CO})\text{Cl}_2(\mu\text{-Cl})](\text{PF}_6)$, 4, in an acetone/methanol/TBAB solution at (A) +50 °C, (B) +25 °C, and (C) -25 °C. The phosphorus resonance denoted by X indicates an impurity.

illustrated below and the product is formulated as $\text{Rh}_2(\mu\text{-dppm})_2\text{Cl}_4(\text{CO})_4$, 16.



The $^{31}\text{P}\{\text{H}\}$ NMR of a CH_2Cl_2 solution of 16 indicates that the complex is stable under an atmosphere of CO , and reverts back to 14 in the absence of a CO atmosphere. Even under a CO atmosphere, 16 decomposes in an acetone solution to yield products that have yet to be characterized. Complex 16 appears to be the chlorine oxidative-addition product analogous to those obtained by treating 2 with Br_2 and I_2 .^{2,7} The fact that 16 is unstable explains yet another reason why it has not been isolated after treating a solution of 2 with elemental chlorine.

When 16 is treated with 1 equivalent of AgPF_6 , two products are obtained.



The major product obtained is 15, and the minor product is 4. The most likely explanation for this observation is that a small amount of 16 loses a mole of CO to form 14, and the reaction with AgPF₆ removes a chloride ligand from both 16 and 14 to form 15 and 4, respectively.

The cyclic voltammogram of 16 in a CH₂Cl₂ solution containing 0.1 M TBAH saturated with CO is shown in Figure 7. The cyclic voltammogram exhibits two cathodic waves at -0.148 and -0.619 V with the corresponding anodic wave at +0.858 V (Figure 7B). When the potential is cycled to an increasingly positive potential, two overlapping irreversible anodic waves at +1.19 and +1.31 V appear with an increase in the cathodic response at -0.15 V (Figure 7A).

Exhaustive bulk electrolysis at -0.7 V indicates approximately 1.7 electrons transferred per rhodium dimer. The cyclic voltammogram of the reduced solution reveals an anodic wave at +0.86 V with the corresponding cathodic wave at -0.61 V (Figure 7C). The product isolated from methanol exhibits CO stretching frequencies at 1976 and 2000 cm⁻¹. The ³¹P(H) NMR spectrum exhibits an AA'A''A'''XX' pattern with a chemical shift of 18.98 ppm and a [¹J_(Rh-P) + ^xJ_(Rh-P)] value of 114.8 Hz, and indicates the presence of PF₆⁻. These data are identical to those of a freshly prepared sample of [Rh₂(μ-dppm)₂(CO)₂(μ-Cl)](PF₆), 1, and thus the reduction product of 16 was characterized as complex 1. The slightly low coulomb count that indicated only 1.7 electrons transferred could possibly result, in part, from a slow reduction of 16

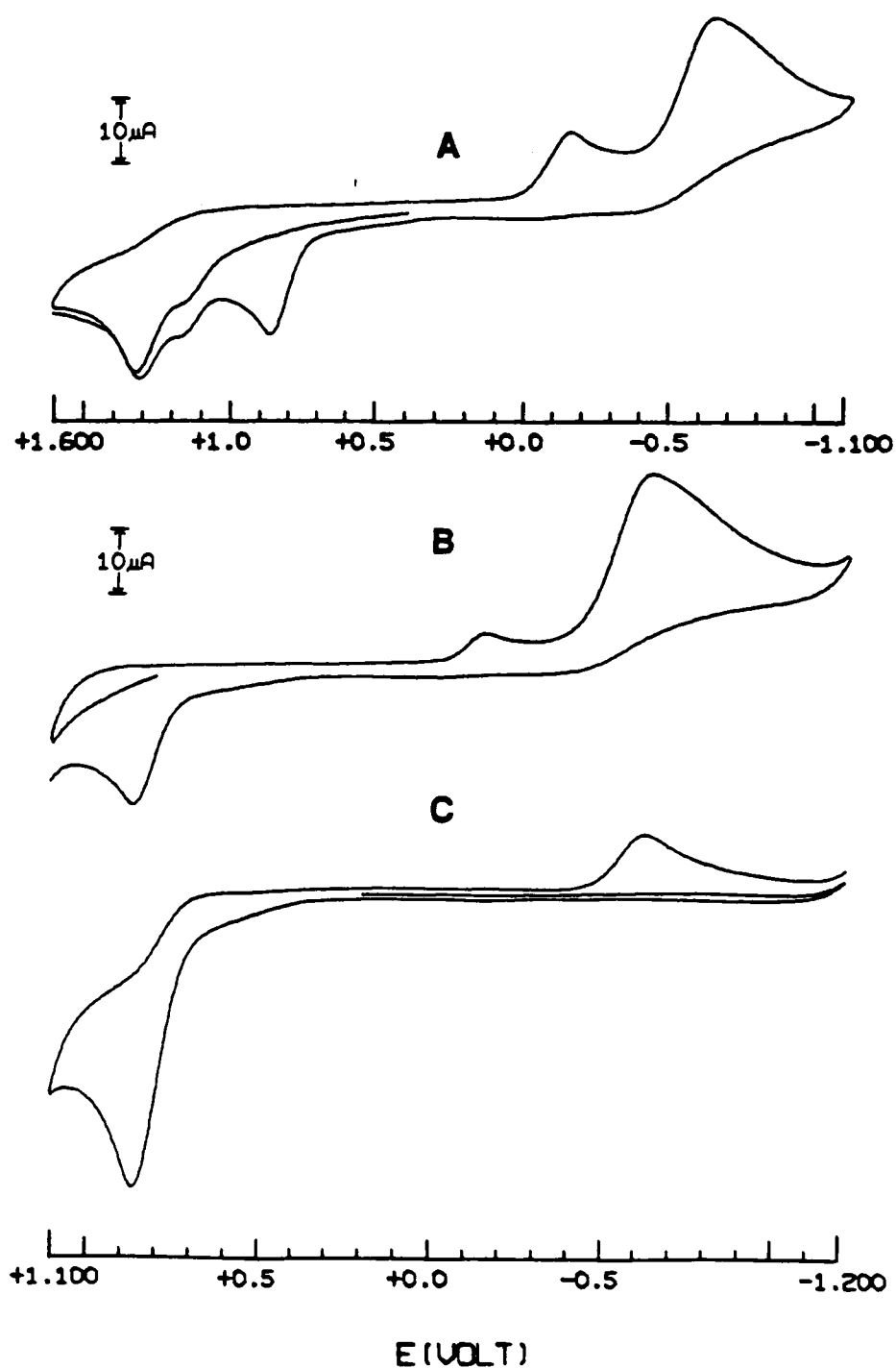


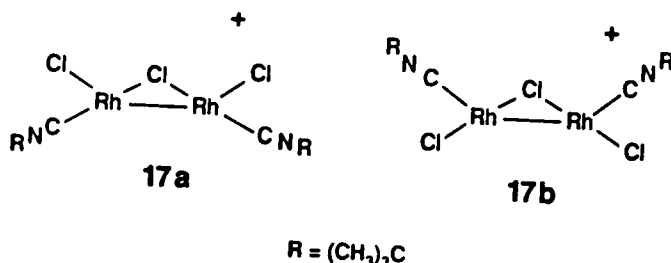
Figure 7. Cyclic voltammograms of 6.8×10^{-4} M $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_4$, **16**, in 0.1 M TBAH/ CH_2Cl_2 /CO (A) before reduction (B) before reduction and (C) after reduction.

by CO. If reduction by CO occurred, this would reduce the number of theoretical coulombs expected and thus the number of electrons transferred per rhodium dimer would be less than two. Reduction by CO is not unreasonable since it was demonstrated earlier that CO reduced 4 and 15 to produce 1 with the stoichiometric amount of chloride ions being detected.

C. Reaction of $[\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-Cl})(\mu\text{-CO})\text{Cl}_2](\text{PF}_6)$ and $[\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-Cl})\text{Cl}_2(\text{CO})_2](\text{PF}_6)$ with $\text{CNC}(\text{CH}_3)_3$

When 4 or 15 is treated with two equivalents of $\text{CNC}(\text{CH}_3)_3$, a new complex is obtained which on the basis of analytical data has been formulated as $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Cl})](\text{PF}_6)$, 17. The IR spectrum of 17 exhibits two bands at frequencies about 60 cm^{-1} higher than those found in $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Cl})(\mu\text{-CO})](\text{PF}_6)$, 3. The higher $\nu(\text{NC})$ in 17, compared to that of 3, is consistent with a higher oxidation state of the rhodium atoms in 17. A higher oxidation state means less π back-bonding and thus a higher NC stretching frequency. The lack of an IR band in either the terminal or the bridging CO stretching region confirms the absence of CO in 17. The presence of a PF_6^- counterion is confirmed by both IR and $^{31}\text{P}(\text{H})$ NMR. The chemical equivalence of the phosphorus atoms is demonstrated by the AA'A''A'''XX' pattern observed in the $^{31}\text{P}(\text{H})$ NMR spectrum. The $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 85.4 Hz suggests the presence of a metal-metal bond. A bridging chloride is postulated on the basis of: (1) the analytical data that show three chloride ions per dimer, (2) four chemically equivalent phosphorus atoms, and (3) the fact that a bridging chloride gives the two

rhodium centers an electron count of 18. Two isomers, 17a and 17b, are potentially possible.



Although the spectroscopic data do not permit an unequivocal identification of the isomer obtained, it has been shown by several structural analyses of trans-bis(dppm)-bridged dirhodium A-frame complexes that the methylene groups of the dppm ligands are folded in a cis position toward the bridging apex ligand. This configuration allows the more bulky phenyl groups to occupy more open sites, and thus minimizes unfavorable intramolecular contacts of the dppm ligands and the apex ligand. This folding of the dppm ligands also creates more open sites opposite the apex ligand and would therefore minimize steric interactions between the phenyl groups and the isocyanide groups occupying position trans to the apex ligand. This would thus favor 17a.

Complex 17 has also been prepared by electrochemical techniques. The cyclic voltammogram of 3 in a medium of $\text{CH}_2\text{Cl}_2/\text{TBAH}/\text{Cl}^-$ exhibits overlapping irreversible oxidation waves at +0.25 and +0.39 V, and associated reduction waves at -0.36, -0.65 and -1.27 V (Figure 8A). Controlled-potential coulometry at +0.55 V indicates that 3 undergoes a two-electron oxidation in the presence of Cl^- . The cyclic voltammogram of the orange oxidized solution exhibits

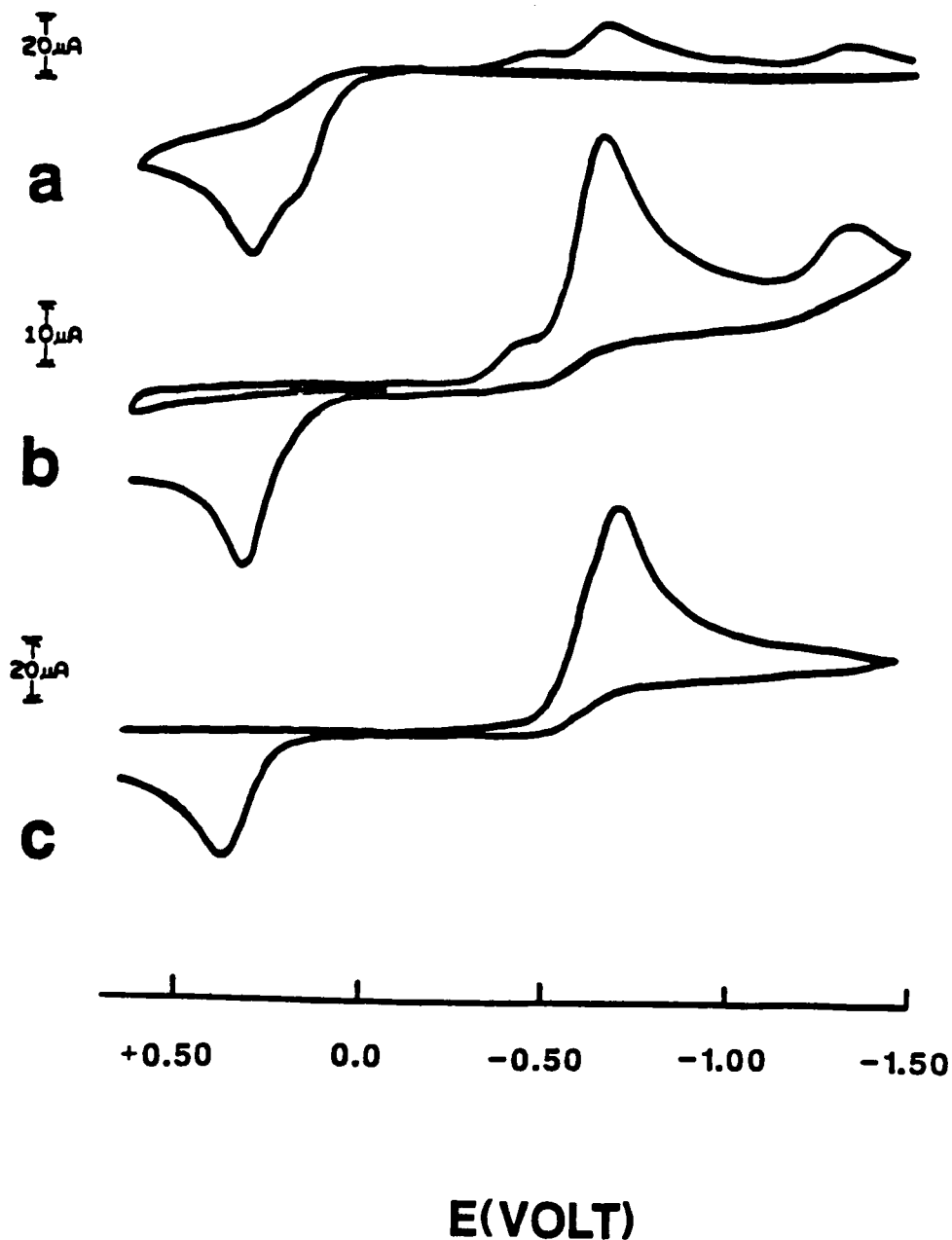
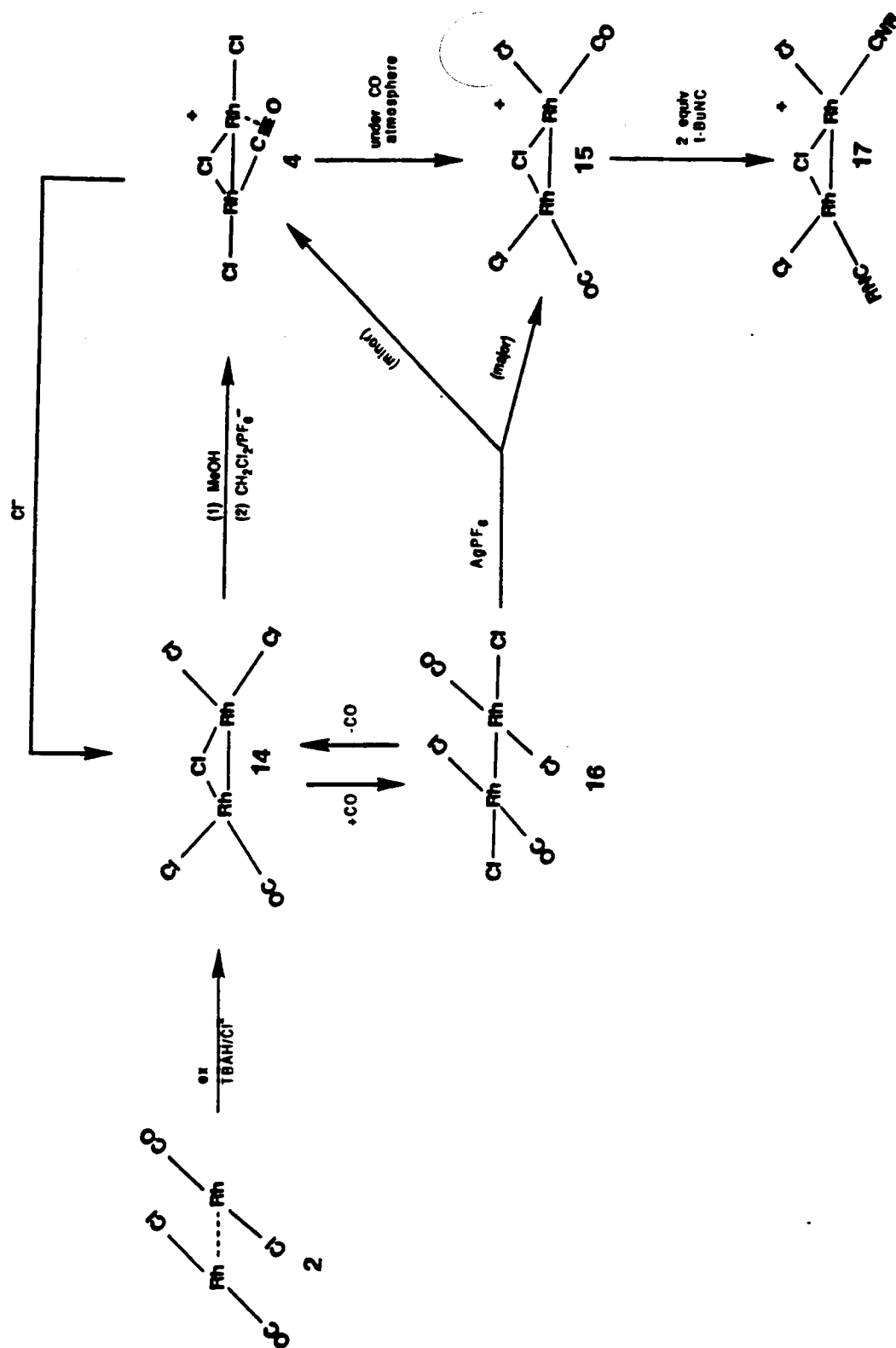


Figure 8. Cyclic voltammograms of 2.2×10^{-4} M $\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-CO})(\mu\text{-Cl})](\text{PF}_6)$, **3**, in CH_2Cl_2 , 0.1 M TBAH, and 1.1×10^{-3} M TBAC (A) before oxidation, (B) after oxidation, and (C) the isolated product, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Cl})\text{Cl}_2](\text{PF}_6)$, **17**, in 0.1 M TBAH/ CH_2Cl_2 .

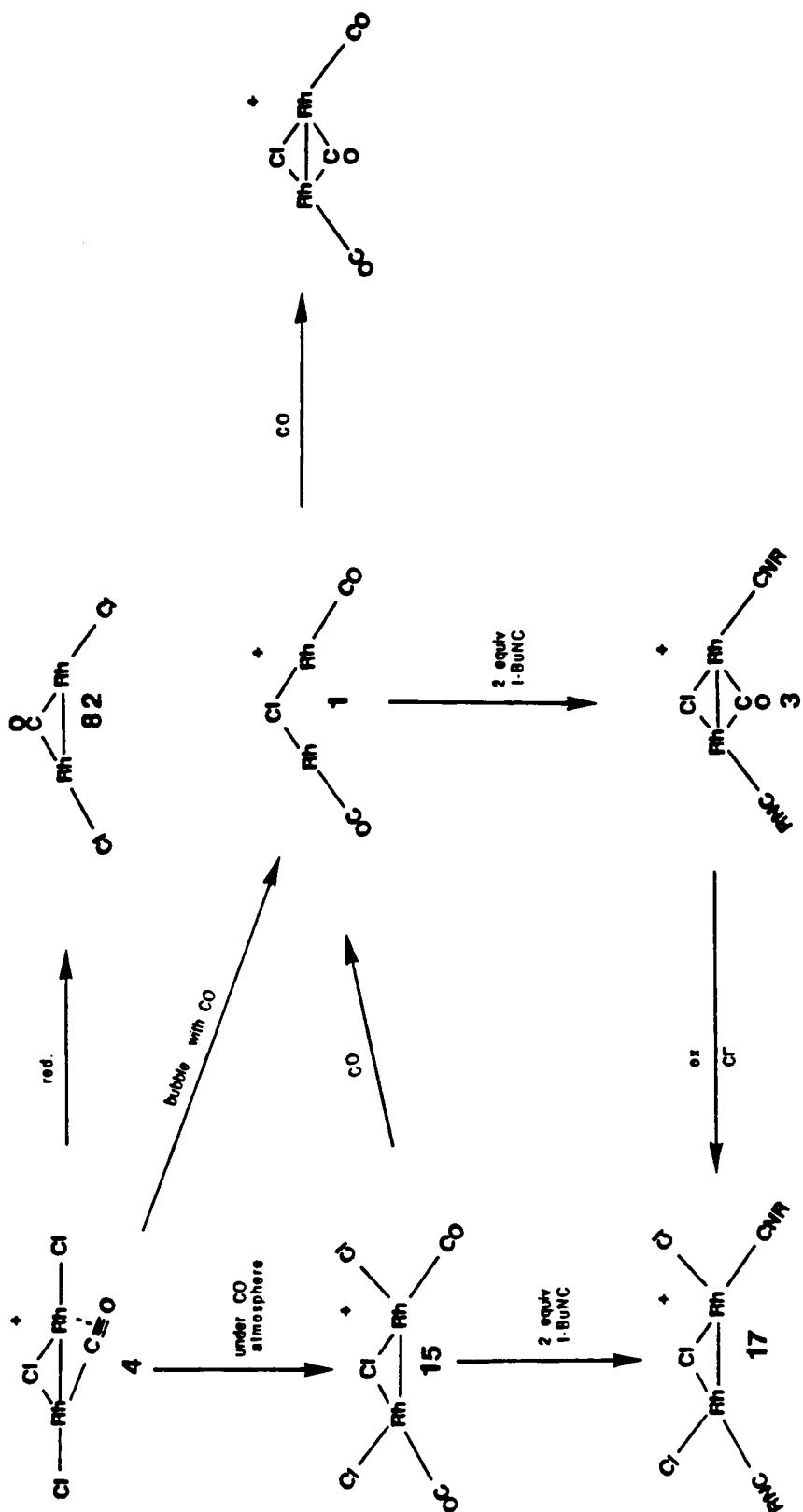
cathodic waves at -0.39, -0.65 and -1.31 V with the corresponding anodic response at +0.40 V (Figure 8B). The reduction waves at -0.39 and -1.31 V (Figure 8B) are apparently due to minor products since the complex isolated from the oxidized solution exhibits only an irreversible reduction wave at -0.69 V. The corresponding oxidation wave of the isolated product occurs at +0.42 V (Figure 8C). The differences in peak potentials of the major oxidation and reduction waves for the isolated product (Figure 8C) and the corresponding waves of the initially oxidized solution (Figure 8B) might be ascribed to the presence of minor products and excess Cl^- in the oxidized solution that are not present in the solution of the isolated product.

An overall reaction scheme relating the chemical and electrochemical behavior of the dinuclear rhodium complexes described in this chapter is summarized in Scheme II.

Scheme II.



Scheme II (continued).

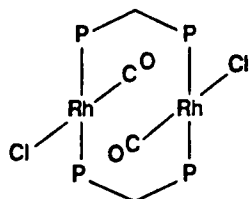


CHAPTER IV

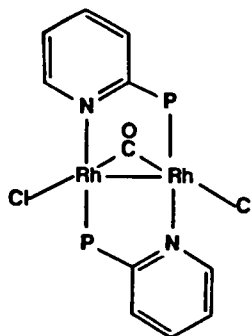
ELECTROCHEMISTRY AND REACTIVITY OF $\text{Rh}_2(\mu\text{-dppp})_2\text{Cl}_2(\mu\text{-CO})$

Interest in dirhodium complexes has warranted investigation of possible factors affecting the nature of the chemical and electrochemical reactivities of some dirhodium complexes with and without metal-metal bonds. The previous chapter discussed some dirhodium complexes containing trans-dppm bridging ligands. The methylene group situated between the coordinating phosphorus atoms allows for a wide range of metal-metal separations, which include some complexes with a formal metal-metal bond and some without a metal-metal bond. However, dinuclear complexes containing trans-dppp ligands limit the metal-metal separation to distances in the single bond range. This restriction is a direct result of the geometric constraints of the two dppp ligands.

The effect of the geometrical constraints is observed when $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ is reacted with dppm and dppp. Treatment of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with dppm leads to the formation of trans- $\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2$, **2**, whereas treatment with dppp generates $\text{Rh}_2(\mu\text{-dppp})_2\text{Cl}_2(\mu\text{-CO})$ **5**.⁸⁰



2



5

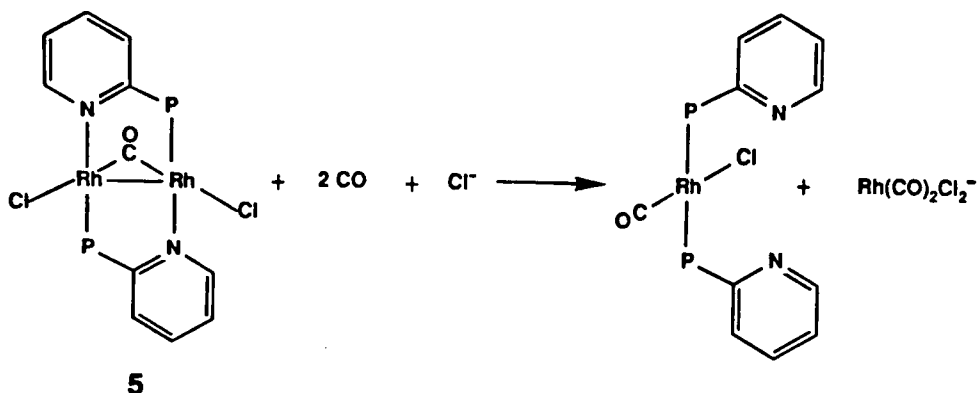
Thus, where many dinuclear Rh(I)-dppm complexes contain no formal Rh-Rh bond, dinuclear Rh(I)-dppp complexes are found to contain a Rh-Rh single bond.

The difference in the bite size of dppp vs dppm has made the investigation of Rh-dppp complexes of interest in determining how the various geometric and steric constraints affect the chemical and electrochemical behaviors of these dinuclear rhodium complexes.

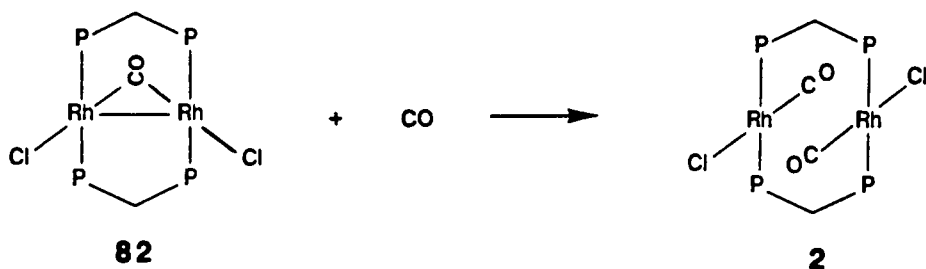
A. Reactivity of $\text{Rh}_2(\mu\text{-dppp})_2\text{Cl}_2(\mu\text{-CO})$
with CO in the presence of Chloride Ions

When a brown solution of 5 is treated with TBAC and bubbled with CO, the solution immediately turns yellow. If the volume is reduced on a rotary evaporator or if the solution is bubbled with Ar, the color of the solution turns to brown-yellow and the $^{31}\text{P(H)}$ NMR spectrum exhibits resonance lines centered at 43.4 ppm which are attributed to 5, and a doublet centered at 29.6 ppm with a splitting of 126.9 Hz. When the solution is again bubbled with CO, it returns to a yellow color, the $^{31}\text{P(H)}$ NMR peaks due to 5 disappear, and only the doublet at 29.6 ppm remains. The IR spectrum of the yellow solution exhibits IR peaks at 2069 and 1991 cm^{-1} . The $^{31}\text{P(H)}$ NMR data and the IR data are consistent with the presence of the monomer, $\text{Rh(dppp)}_2(\text{CO})\text{Cl}^{62}$, and the anion, $\text{Rh(CO)}_2\text{Cl}_2^-$.⁶⁶ The reaction is outlined in Equation 1, and is consistent with the observation that addition of either CO or Cl^- alone does not afford the products shown in Equation 1.

Equation 1.



This reaction is somewhat interesting in light of the fact that the dppm complex analogous to 5, 82, affords the face-to-face dimer 2 when treated with CO.¹⁰



Besides possible electronic factors, one factor which almost certainly plays a role in establishing these differences is the difference in bite sizes of the two ligands and the metal-metal distances they can accommodate. If by the addition of a CO molecule 5 were to form a face-to-face complex similar to 2, the small bite size of the dppp ligand would dictate a metal-metal bond. The existence of a metal-metal bond in such a structure for a dppp Rh(I)-Rh(I) species would result in the metal centers being

17-electron paramagnetic centers and less stable than the corresponding d^8 square planar 16-electron metal centers in 2. Therefore, as illustrated in Equation 1, the breakdown of such a dimer into monomeric species is favored over the conversion of the bridging CO to a terminal CO with concomitant addition of CO or Cl^- to form the dinuclear species analogous to 2.

B. Electrochemistry of $Rh_2(\mu\text{-dppp})_2Cl_2(\mu\text{-CO})$ in TBAN

The cyclic voltammogram of 5 in a CH_2Cl_2 solution containing 0.1 M TBAN exhibits an irreversible oxidation peak at +0.90 V and a corresponding reduction peak at -0.82 V (Figure 9A). Controlled-potential coulometry at +1.0 V indicates a two-electron process apparently leading to a Rh(II)-Rh(II) dimer. The oxidation product gives rise to a reduction wave at -0.89 V with the corresponding anodic wave at +0.84 V (Figure 9B).

The cyclic voltammogram of 5 in a CH_2Cl_2 solution containing 0.1 M TBAN and excess chloride reveals an irreversible anodic wave at +0.97 V and a cathodic wave at -0.70 V (Figure 9C). Bulk electrolysis results in a two-electron transfer with the oxidized solution exhibiting a cathodic wave at -0.84 V, and an anodic wave at +0.84 V (Figure 9D).

Identical products are obtained from the two electrolysis media, CH_2Cl_2 /TBAN (30%) and CH_2Cl_2 /TBAN/TBAC (70%); however, the CH_2Cl_2 /TBAN medium also affords a brown product which has eluded characterization. The IR spectrum of the green solid exhibits a carbonyl stretching frequency at 2054 cm^{-1} , indicating the presence

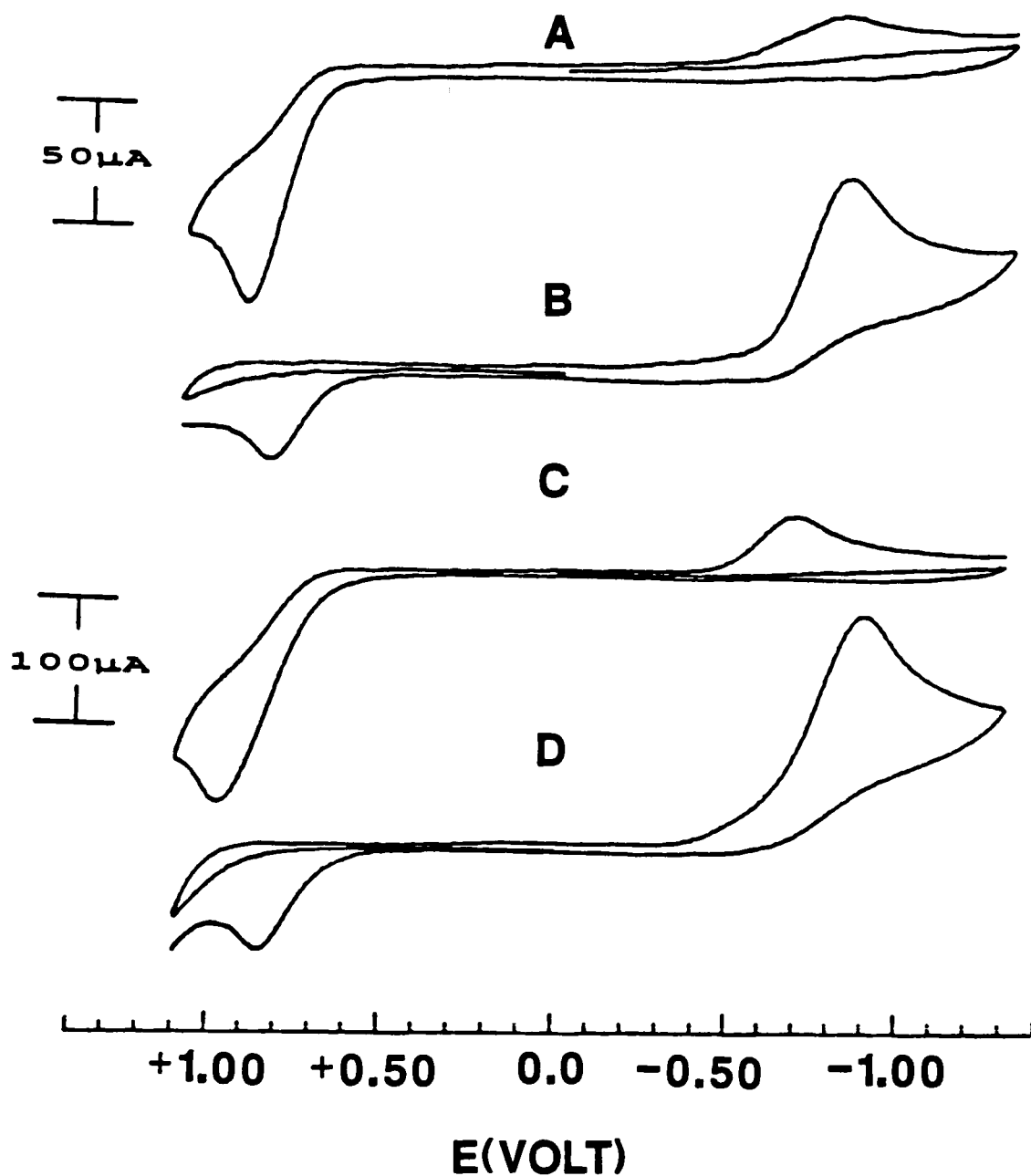


Figure 9. Cyclic voltammograms of 10^{-4} M $\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-CO})\text{Cl}_2$, 5, in 0.1 M TBAN/ CH_2Cl_2 (A) before oxidation, (B) after oxidation, (C) before oxidation in the presence of 5.0×10^{-4} M TBAC, and (D) after oxidation in the presence of TBAC.

of a terminal carbonyl ligand. The presence of a terminal CO means that the two rhodium environments are different, and therefore, the environments of the two phosphorus atoms in the two bridging dppp ligands are different.

The $^{31}\text{P(H)}$ NMR spectrum of the Rh(II) dimer consists of two doublets-of-doublets with chemical shifts of 33.0 and 28.7 ppm. The larger coupling constant, $^1J_{(\text{P-Rh})}$, for the downfield multiplet is 114.7 Hz and that for the upfield multiplet is 119.6 Hz. The smaller splitting in each case is 17.1 Hz (Figure 10A). In order to assign the phosphorus resonance, the complex was prepared with ^{13}C -enriched CO. Only the downfield doublet-of-doublets exhibits the effect of ^{13}C coupling (Figure 10B), indicating that the CO and the phosphorus nucleus giving rise to the downfield multiplet are coordinated to the same rhodium atom. With ^{13}CO , the downfield doublet-of-doublets appears as a pseudo-doublet of triplets since the $^2J_{(\text{P-C})}$ value of 14.6 Hz is close enough to the smaller coupling of the downfield multiplet so that the two center lines of the new doublet overlap and give rise to a three-line pattern.

The isotope effect is also revealed in the CO stretching frequency with a decrease in the CO band from 2054 to 2006 cm^{-1} for the ^{13}CO analogue.

The structure of the oxidized product was confirmed by single crystal structural analysis to be $\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-NO}_3)\text{COCl}_3$, 7.⁸⁴ Ruby-colored prismatic crystals of 7 were grown by slow diffusion of ether into a CH_2Cl_2 solution of 7.

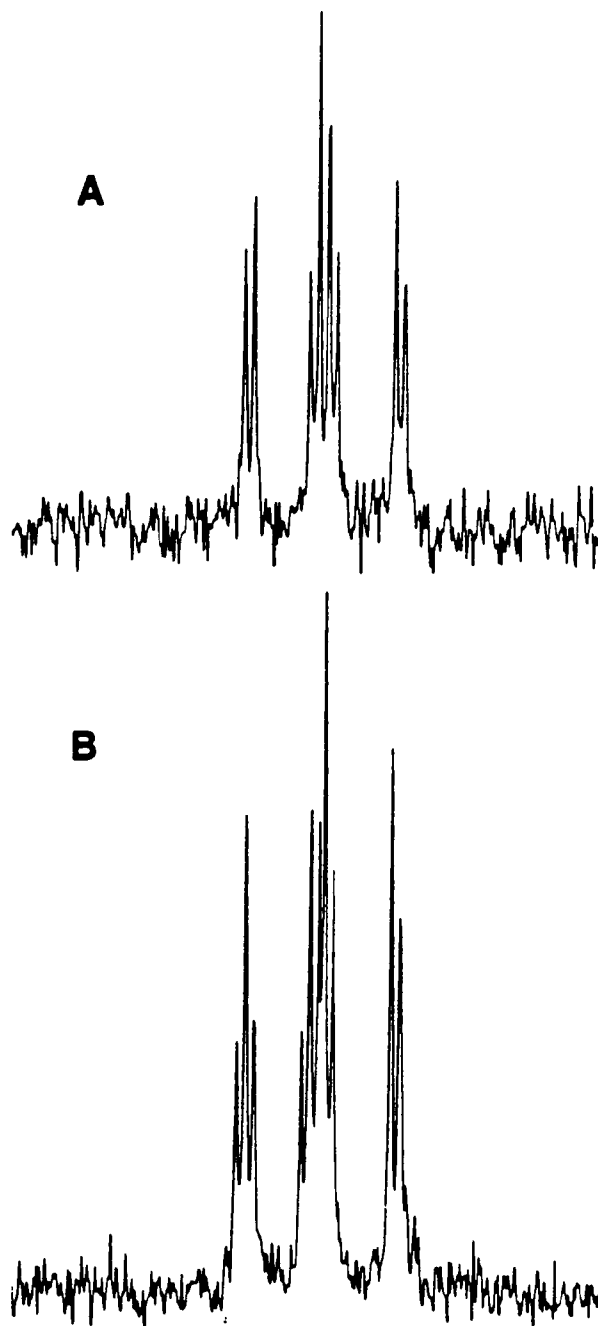


Figure 10. The $^{31}\text{P}\{\text{H}\}$ NMR spectra of (A) $\text{Rh}_2(\mu\text{-dppp})_2\text{COCl}_3(\mu\text{-NO}_3)$, 7, and (B) $\text{Rh}_2(\mu\text{-dppp})_2^{13}\text{COCl}_3(\mu\text{-NO}_3)$, 8.

An ORTEP plot of the dinuclear species with the atomic numbering scheme is shown in Figure 11. Complex 7 contains two Rh(II) d^7 metal centers surrounded by ligating atoms that form two interpenetrating irregular octahedra held together by the two bridging transoid dppp ligands in a head-to-tail arrangement, a bridging nitrate ion, and a metal-metal bond. Each rhodium atom is located in the center of an irregular octahedron such that each Rh occupies a vertex of the octahedron surrounding the other Rh atom. A chlorine atom is coordinated to each rhodium atom such that the two chlorine atoms are tilted away from the Rh-Rh vector toward the bridging nitrate by 10° . One rhodium atom is located at the intersection of two essentially perpendicular (179.5°) vectors, a PRhN vector (P and N from two transoid dppp ligands) and an ORhCO vector (O from $\mu\text{-NO}_3$). The second rhodium is also located at the intersection of two essentially perpendicular (178.9°) vectors, a PRhN vector and an ORhCl vector (O from $\mu\text{-NO}_3$). When 7 is viewed down the Rh-Rh axis, it is seen that the ligating atoms on the two metals are in a staggered orientation with a torsional angle of 13.79° (Figure 12). The skewing of the PRhN units is not surprising since the A-frame precursor, $\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-CO})\text{Cl}_2$, exhibits significant skewing of the PRhN units.⁶³ This skewing has been related to the bite of the dppp ligand. An idealized Rh-Rh separation of $2.35 \text{ \AA}$ has been determined for a planar $(\text{dppp})_2\text{M}_2$ unit in which each dppp ligand bridges the two metal atoms.⁶³ The skewing in 7 is undoubtedly induced by the metal-metal bond distance of $2.589 \text{ \AA}$. This distance is shorter than the metal-metal distance

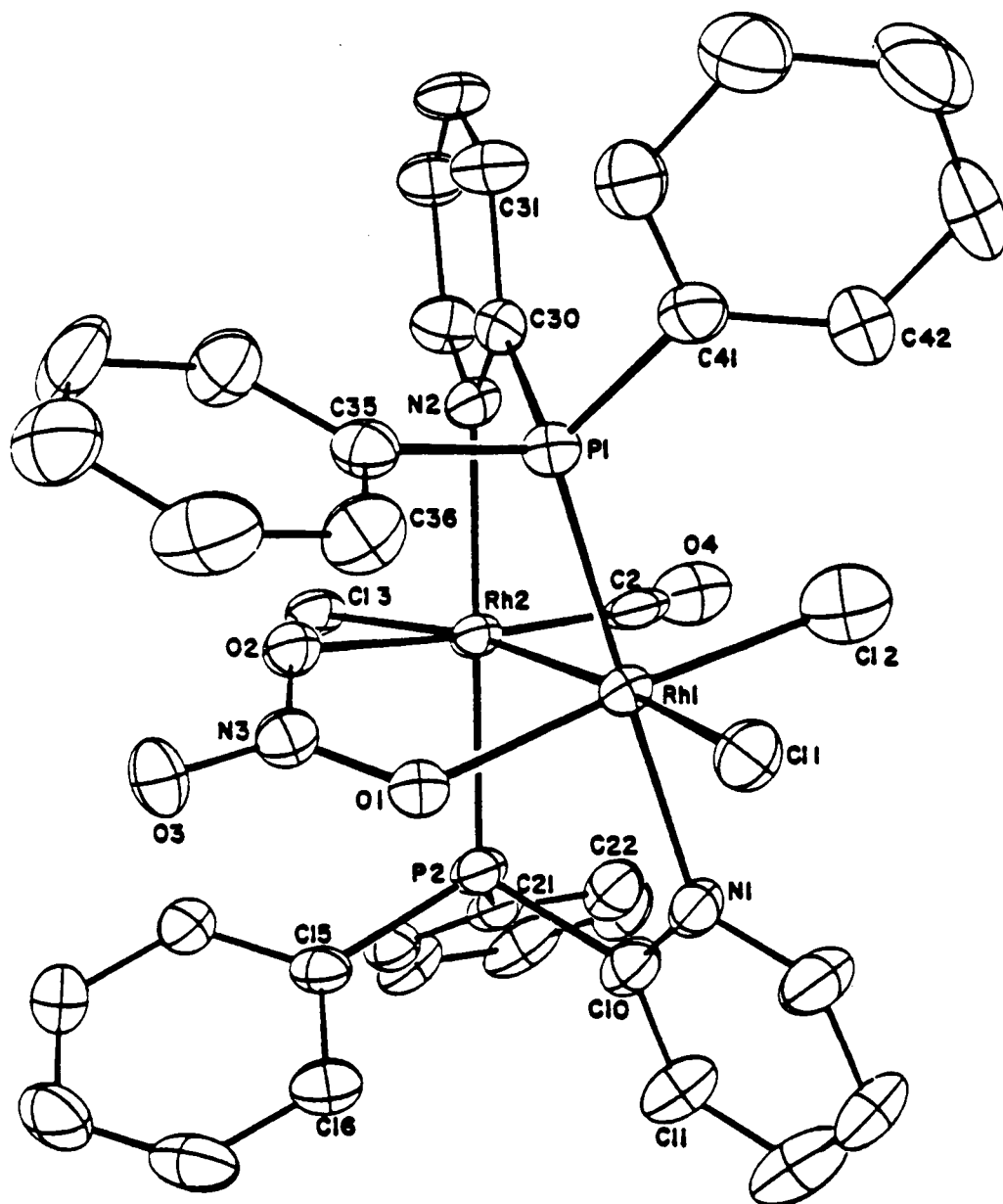


Figure 11. ORTEP plot of $\text{Rh}_2(\mu\text{-dppp})_2\text{COCl}_3(\mu\text{-NO}_3)$, Z , showing the numbering scheme.

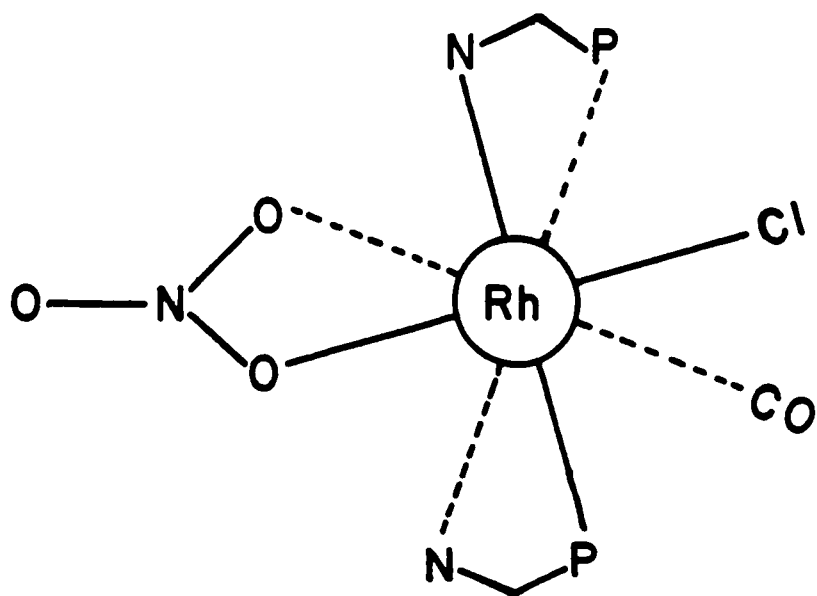


Figure 12. A view down the Rh-Rh vector of $\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-CO})\text{Cl}_3(\mu\text{-NO}_3)$, **1**, showing the skewing of the dppp ligands.

of 2.612 Å observed for the A-frame rhodium(I) precursor. This decrease in Rh-Rh bond distance apparently results from the increase in metal-metal bonding interactions that occur upon removal of electrons from essentially a $d_{z^2}(\sigma^*)$ orbital during the oxidation of the metal centers.

The only anomalous feature of the structure is the C-O distance of the carbonyl group. The anomalous value of 0.835 Å results from a disorder involving the CO on one rhodium atom and the staggered Cl on the second rhodium atom. A similar type of disorder involving trans carbonyl and chloro ligands on the same rhodium atom has previously been observed.⁸⁵ The disorder in **7** apparently results when some molecules crystallize with the carbonyl and chloro ligands having exchanged coordination sites. This can be achieved by simply rotating the molecule 180° about a vector bisecting the Rh-Rh bond and the O(1)-N(3)-O(2) angle. A model consisting of a half Cl and a half CO at each site fits the data as well as the one with the CO totally contained in one site and the Cl in the other site. Because of this disorder the C-O and the Rh(1)-Cl(2) distances could not be determined accurately.

The formation of **7** from the oxidation of **5** in TBAN/TBAC is somewhat interesting; although Cl^- is generally considered to be a better coordinating ligand for transition metals than NO_3^- , the dinuclear Rh(I) species adds a Cl^- and a NO_3^- instead of two Cl^- ions. It is also noteworthy that even in the absence of an external source of chloride ions, oxidation of **5** in the CH_2Cl_2 /TBAN medium still yields **7**. Either the starting material or some other

rhodium-containing species serves as the source of the additional chloride found in 7. This is apparently the reason for the lower yield of 7 under these conditions. The solvent, CH_2Cl_2 , is not the source of Cl^- since the same results are obtained with the medium $(\text{CH}_3)_2\text{CO}/\text{TBAH}$.

The addition of a bridging nitrate ion, instead of a bridging chloride ion, may result from the ability of the bridging nitrate to better accommodate the twist angle (see Figure 11) imposed by the dppp ligands while still allowing each rhodium atom to have an electron count of 18.

C. Electrochemistry of $\text{Rh}_2(\mu\text{-dppp})_2\text{Cl}_2(\mu\text{-CO})$
in TBAH

The cyclic voltammogram of 5 in $\text{CH}_2\text{Cl}_2/\text{TBAH}$, shown in Figure 13A, exhibits two overlapping irreversible oxidation waves at +0.87 and +1.36 V, with the cathodic response at -0.07 V. Controlled-potential coulometry at +1.0 V indicates that two electrons are transferred per dinuclear species, and suggests that each irreversible oxidation is a one-electron process. The cyclic voltammogram of the oxidized solution exhibits two cathodic waves at -0.52 and -0.81 V with the corresponding anodic wave at +0.78 V.

Although a two-electron controlled-potential electrolysis has not afforded an isolateable oxidation product, the results do indicate that the oxidation product formed on the voltammetric time scale undergoes a follow-up transformation during electrolysis. These data suggest that a reactive $\text{Rh(II)}\text{-Rh(II)}$ species is initially formed during the electrolysis. The propensity of Rh(II)

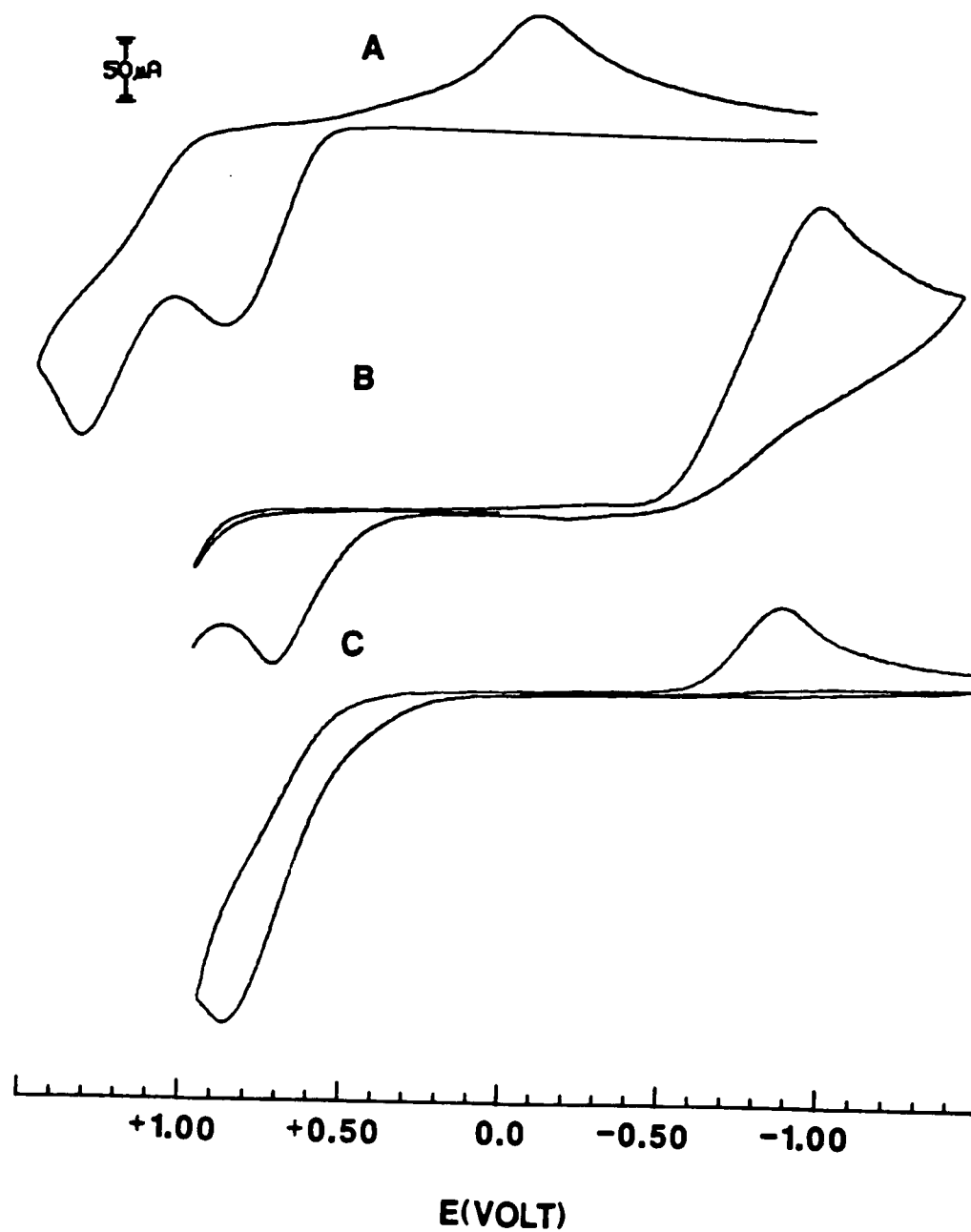


Figure 13. Cyclic voltammograms of 2.2×10^{-4} M $\text{Rh}_2(\mu\text{-dppp})_2(\mu\text{-CO})\text{Cl}_2$, 5, (A) in TBAH/ CH_2Cl_2 , (B) after oxidation in TBAH/ CH_2Cl_2 and 1.1×10^{-3} M TBAC, and (C) before oxidation in TBAH/ CH_2Cl_2 /TBAC.

to acquire a higher coordination number than that favored for Rh(I) is likely responsible, in part, for the follow-up chemical process.

The propensity of Rh(II) species to attain a higher coordination number is demonstrated by a shift in the cathodic peak potential toward more negative potentials when coordinating species are present. The cyclic voltammogram of 5 in a 1:1 mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ containing 0.1 M TBAH reveals an anodic wave at +0.63 V, with corresponding cathodic responses at -0.22, -0.43 and -0.97 V. The coordinating ability and basicity of CH_3CN results in CH_3CN facilitating the removal of both electrons from 5, and a shift of the cathodic peak potentials to more negative values. In the presence of CH_3CN , the oxidized product formed is more stable to reduction than the oxidized product generated in the absence of CH_3CN . Controlled-potential coulometry at +0.80 V indicates that the oxidation process is a two-electron process. The cyclic voltammogram of the oxidized solution reveals cathodic waves at -0.27, -0.42, -0.59 and -0.98 V, and the corresponding anodic wave at +0.69 V. The similar potentials obtained before and after bulk oxidation indicate that the product formed on the cyclic voltammetric and the product formed on the bulk electrolysis time scale are alike. This is in contrast to the results observed for the analogous oxidation in CH_2Cl_2 , emphasizing the stability of dirhodium(II) complexes generated in the presence of coordinating species.

The cyclic voltammetric behavior of 5 in $\text{CH}_2\text{Cl}_2/\text{TBAH}/\text{Cl}^-$ is illustrated in Figure 13C. An irreversible oxidation occurs at

+0.90 V, just before the onset of the oxidation wave for Cl^- . The cathodic response occurs at -0.90 V. These results also indicate that the oxidation product formed on the voltammetric time scale in the presence of Cl^- is more stable to reduction than that formed in the absence of Cl^- . Controlled-potential oxidation at +0.90 V involves a transfer of two electrons per dinuclear unit, and thus involves the formation of a Rh(II)-Rh(II) species. The cyclic voltammogram of the oxidized solution exhibits an irreversible reduction wave at -0.98 V and an associated anodic response at +0.84 V (Figure 13B). The electrochemical oxidation product obtained from the $\text{CH}_2\text{Cl}_2/\text{TBAH}/\text{Cl}^-$ medium exhibits an IR band at 2044 cm^{-1} after recrystallization from CH_2Cl_2 which indicates the presence of a terminal CO. When the product is isolated from acetone, it gives a strong IR band at 2044 cm^{-1} and a weak band at 1805 cm^{-1} . The product containing C-13 enriched CO exhibits a $\nu(\text{CO})$ value of 1998 cm^{-1} after isolation from CH_2Cl_2 and $1998(\text{s})$, and $1765(\text{w})\text{ cm}^{-1}$ when isolated from acetone. These data indicate that in acetone a small amount of product contains a bridging CO. An acetone band at 1715 cm^{-1} is also observed in the IR spectra from the products isolated from acetone.

At 25°C , the $^{31}\text{P}\{\text{H}\}$ NMR spectrum of the oxidation product exhibits the broad peak shown in Figure 14A. When the temperature is lowered to 0°C , four peaks are apparent (Figure 14B). Further splitting of the peaks is observed at -25°C (Figure 14C). The spectrum at -25°C is interpreted as that resulting from two phosphorus atoms in different environments with chemical shifts of 29.7

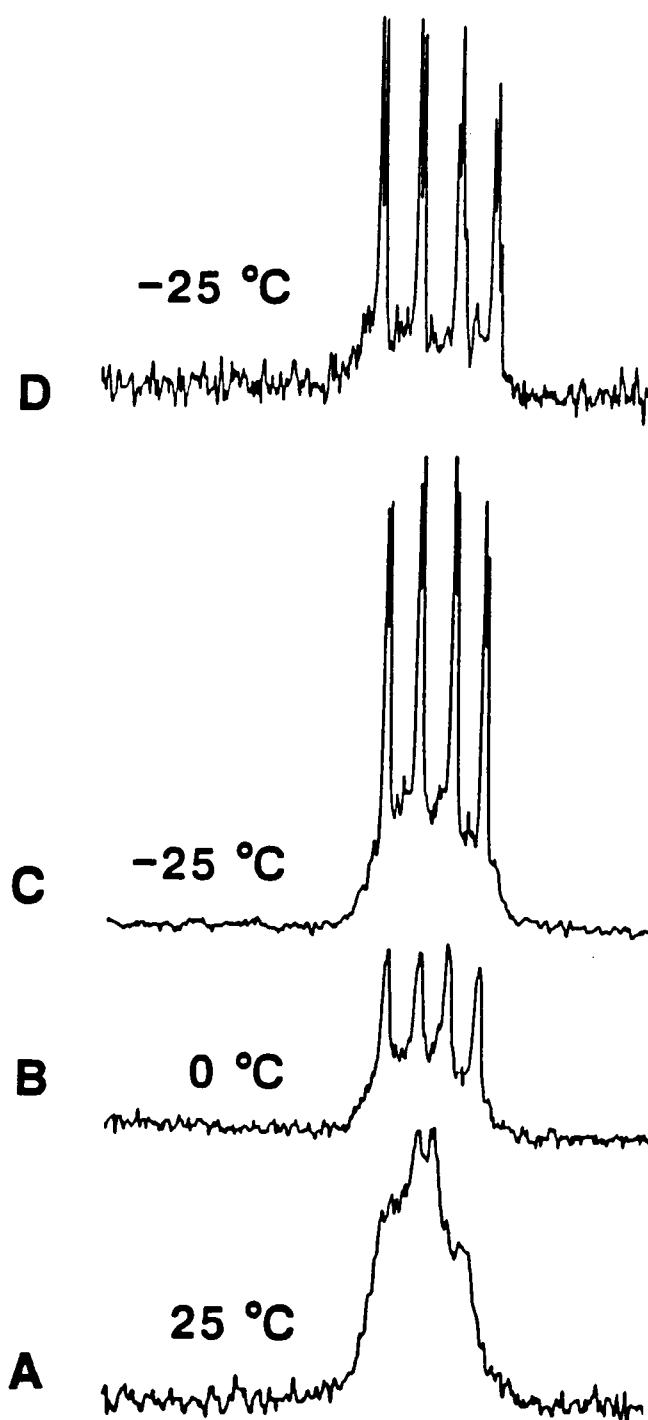
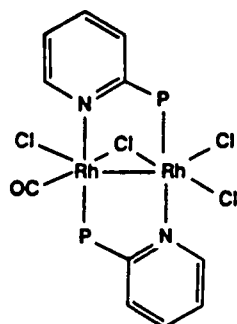


Figure 14. Variable-temperature $^{31}\text{P(H)}$ NMR spectra of $\text{Rh}_2(\mu\text{-dppp})_2(\text{CO})(\mu\text{-Cl})\text{Cl}_3$, 14, at (A) +25 °C, (B) 0 °C, (C) -25 °C and (D) -25 °C (^{13}C enriched).

and 23.2 ppm. The phosphorus atom giving rise to the low-field resonance exhibits a one-bond Rh (^{103}Rh , $I=1/2$; 100%) coupling of 117.2 Hz and a two-bond Rh coupling of 14.7 Hz. The phosphorus atom giving rise to the high-field resonance exhibits a one-bond Rh coupling of 109.9 Hz and a two-bond Rh coupling of 12.2 Hz.

The analytical data of the oxidation product of 5, isolated from CH_2Cl_2 , resulted in the formulation of the product as $\text{Rh}_2(\mu\text{-dppp})_2(\text{CO})(\mu\text{-Cl})\text{Cl}_3$, 9. This product can also be prepared by treating a CH_2Cl_2 solution of 5 with elemental chlorine at -78°C . Based on the low temperature $^{31}\text{P}\{\text{H}\}$ NMR, IR, and analytical data, 9 is assigned the structure illustrated by IV.

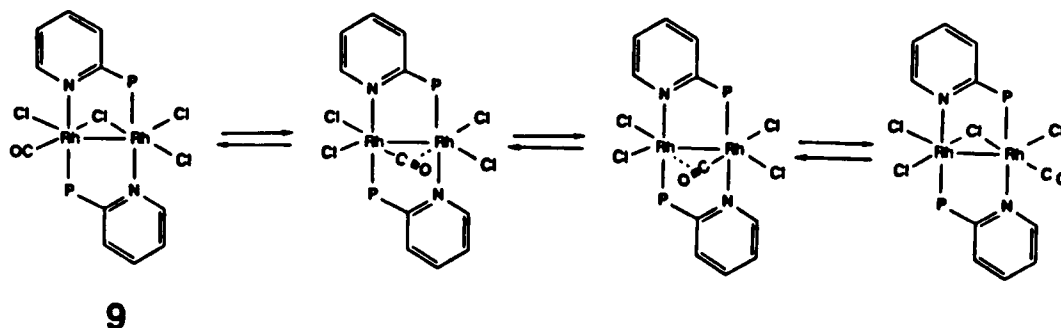


IV

The bridging Cl^- is postulated on the basis of an electron count of 18 for each metal center.

The variable-temperature $^{31}\text{P}\{\text{H}\}$ NMR spectra shown in Figure 14 indicate that 9 is fluxional, and the weak IR peak attributable to a bridging CO in acetone suggest that the fluxional process involves bridging CO. A feasible fluxional behavior is described by the interconversion outlined in Scheme III.

Scheme III.



The initial bridging CO species is postulated to be one with a semi-bridging CO. This is based on the fact that in this mode the CO is a four-electron donor, and thus the 18-electron configuration at each metal center is maintained and the metal-metal bond is also maintained. A symmetrically bridged CO would act as a two-electron donor and would require the loss of the metal-metal bond, a process which is not favored for the dppp ligand, though the symmetrically-bridged CO species might be a transient species formed in the interconversion of the two semi-bridged CO species shown in Scheme III. The $^{31}\text{P(H)}$ NMR spectrum of **9** in 1,2-dichloroethane at 75 °C exhibits two major lines centered at 27.6 ppm that appear to be the components of a doublet compared to that shown in Figure 14 at 25 °C. The signal-to-noise ratio for the spectrum in 1,2-dichloroethane was less than ideal due to limitations of solubility. At high temperatures the spectrum is approaching that of two phosphorus atoms in equivalent averaged environments and exhibiting rhodium-phosphorus coupling (ca. 124.5 Hz at 75 °C). The peak separation is well

within the range of the rhodium-phosphorus coupling expected for these types of species.

Without the C-13 enriched species it was not possible to unequivocally assign the phosphorus resonances. Figure 14D clearly indicates that in 9 the phosphorus atom bonded to the rhodium containing the CO gives rise to the resonance at 23.2 ppm. The pseudo-triplet results from the fact that the coupling constants, $^2J_{P-C}$ and $^2J_{P-Rh}$, are both 12.2 Hz. Similar experiments have shown that the phosphorus atom bonded to the CO-containing Rh in the analogous nitrate-bridged complex exhibits a resonance at 33.0 ppm. Since the chemical shifts for the phosphorus atom bonded to the rhodium atoms containing two Cl^- are close for 9 (29.7 ppm) and 7 (28.7 ppm), it is clear that the electronic environment of the CO-bonded rhodium atom is much more susceptible to the structural and electronic requirements of the bridging chloro and nitrate ligands, probably because of variations in the extent of back-bonding with the π^* orbitals of CO. A stick diagram, shown in Figure 15, clearly demonstrates that the CO-bonded rhodium atoms in 9 and 7 are strongly affected by the bridging moiety, and the rhodium atoms containing two terminal chloride ligands are not.

Although electrolysis of 5 in a CH_2Cl_2 solution containing TBAN and excess Cl^- generates 7, treatment or refluxing a CH_2Cl_2 solution of 9 in the presence of excess nitrate does not result in the replacement of a chloride ligand with nitrate to produce 7.

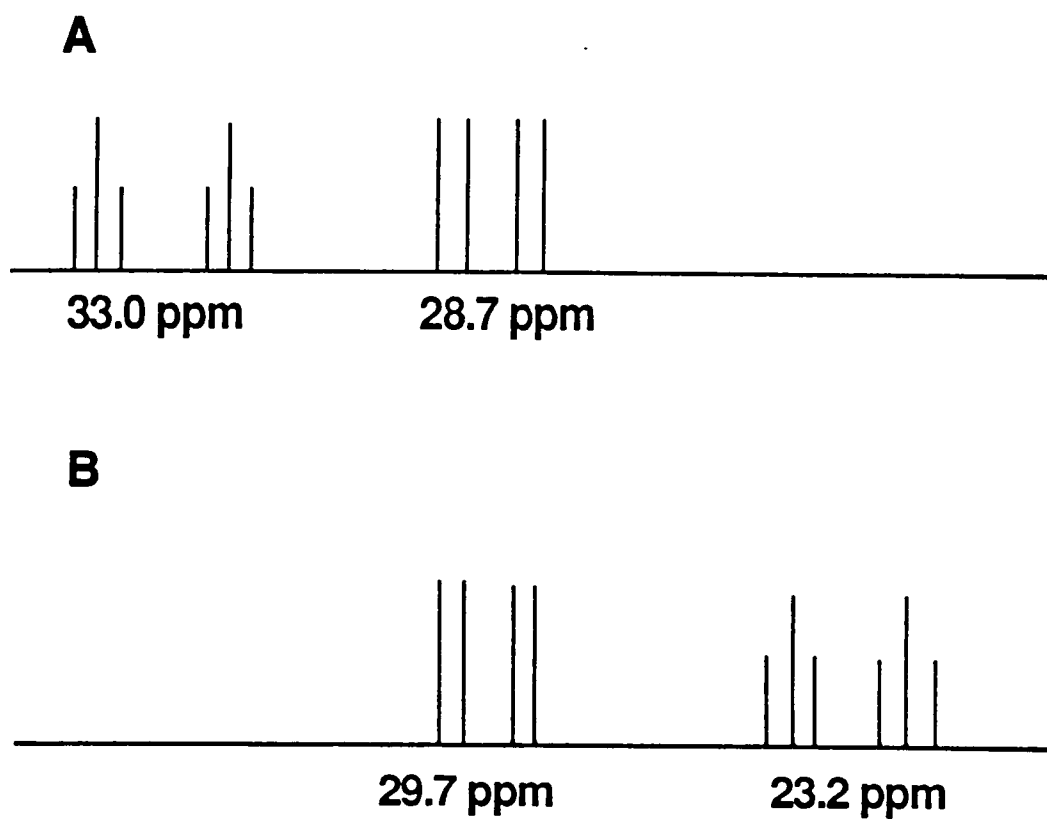
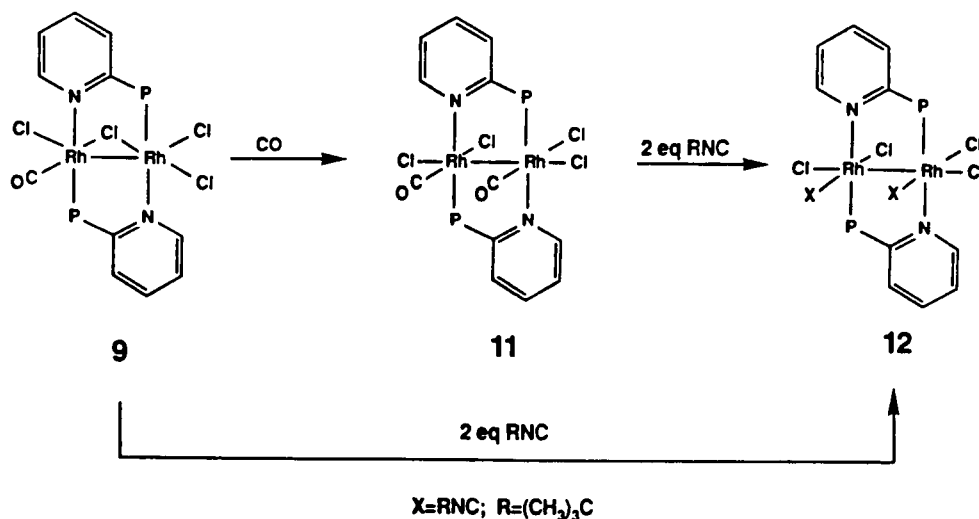


Figure 15. A stick diagram of the $^{31}\text{P(H)}$ NMR of (A) $\text{Rh}_2(\mu\text{-dppp})_2^{13}\text{COCl}_3(\mu\text{-NO}_3)$, 12 and (B) $\text{Rh}_2(\mu\text{-dppp})_2^{13}\text{CO}(\mu\text{-Cl})\text{Cl}_3$, 14.

D. Reaction of $\text{Rh}_2(\mu\text{-dppp})_2\text{Cl}_3(\mu\text{-Cl})\text{CO}$
with CO and $t\text{-BuNC}$

Bubbling a CH_2Cl_2 solution of **9** with carbon monoxide results in a color change from brown to orange with the isolation of an orange solid. This product exhibits strong and medium IR bands at 2066 cm^{-1} and 2039 cm^{-1} , respectively, which indicate the presence of terminal CO molecules. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of the product exhibits a doublet at 22.4 ppm with $J_{\text{Rh-P}} = 109.9\text{ Hz}$. The spin system is $\text{AA}'\text{XX}'$, thus the long-range couplings must be such that the pattern appears as that of a simple AX system. The CO addition product is formulated as $\text{Rh}_2(\mu\text{-dppp})_2(\text{CO})_2\text{Cl}_4$, **11** (Scheme IV). Complex **11** is stable in the solid and solution whereas the dppm analogue loses a molecule of CO if it is not kept under an atmosphere of CO.

Scheme IV.



Treatment of 9 or 11 with t-BuNC, as outlined in Scheme IV, affords a product that exhibits a weak IR band at 2218 cm^{-1} and a strong band at 2189 cm^{-1} which have been assigned to $\nu(\text{NC})$ of the complex $\text{Rh}_2(\mu\text{-dppp})_2(\text{t-BuNC})_2\text{Cl}_4$, 12. The $^{31}\text{P}(\text{H})$ NMR spectrum of 12, shown in Figure 16, is more complex than the simple doublet observed for 11. Though the spectrum of 12 is symmetrical, each component of the doublet is split into several lines. This difference indicates that the long-range couplings for the AA'XX' systems are much more prominent for 12 than for 11. This undoubtedly results, in part, from the different electronic environments of the metal centers due to differences in the bonding properties of the CO and t-BuNC ligands. The more complex NMR spectrum for 12 may also result in part from averaged coupling of two or more species in equilibrium. Variable-temperature $^{31}\text{P}(\text{H})$ NMR experiments from -85 to $+50\text{ }^\circ\text{C}$ do show that the relative intensities of the phosphorus resonance lines of 12 vary with temperature.

Some Cl^- is detected in a CH_2Cl_2 solution of 12 with a chloride ion selective electrode. This result is interpreted to mean that the nonionic dinuclear species, 12, is in equilibrium with a dirhodium cation and a Cl^- . Addition of NH_4PF_6 in methanol to a CH_2Cl_2 solution of 12 gives a product whose IR spectrum contains a strong band at 2189 cm^{-1} and a weak shoulder at 2225 cm^{-1} , in addition to PF_6^- bands at 839 and 557 cm^{-1} . The $^{31}\text{P}(\text{H})$ NMR spectrum of this product is more like that of 11 than 12 since it exhibits a doublet at 25.3 ppm with a splitting of 113.0 Hz . The product is

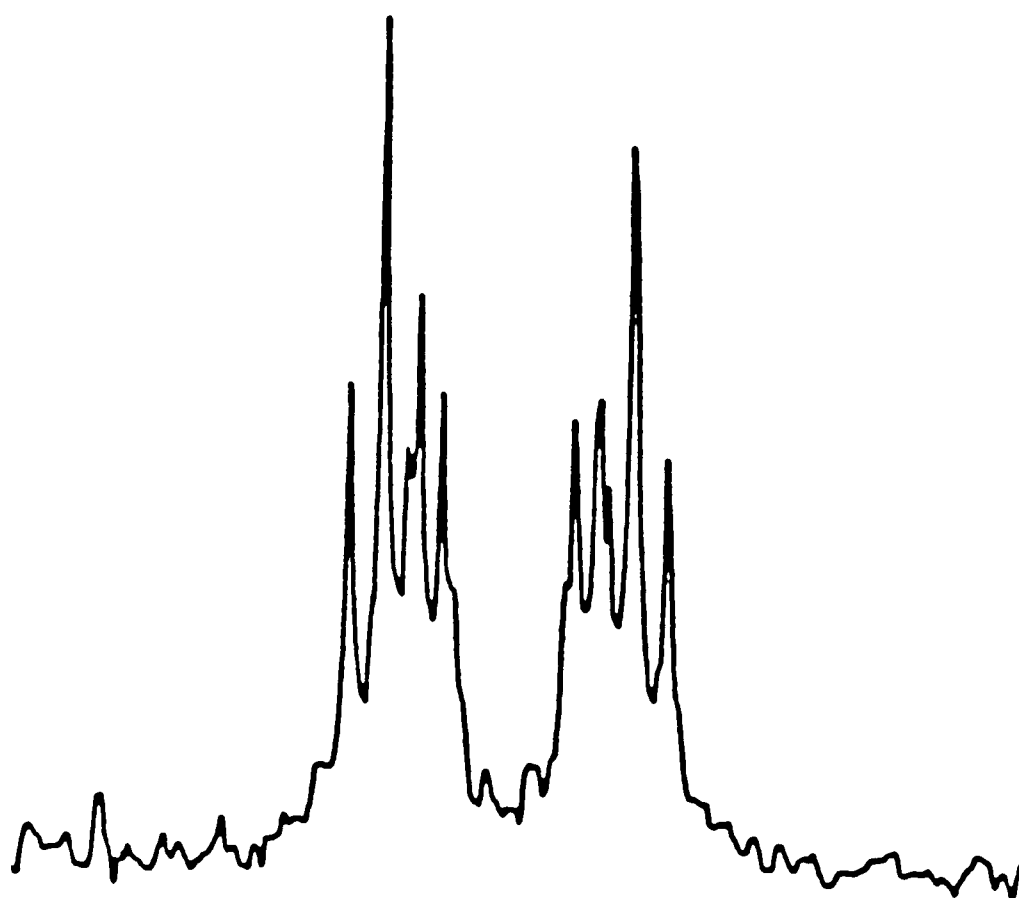
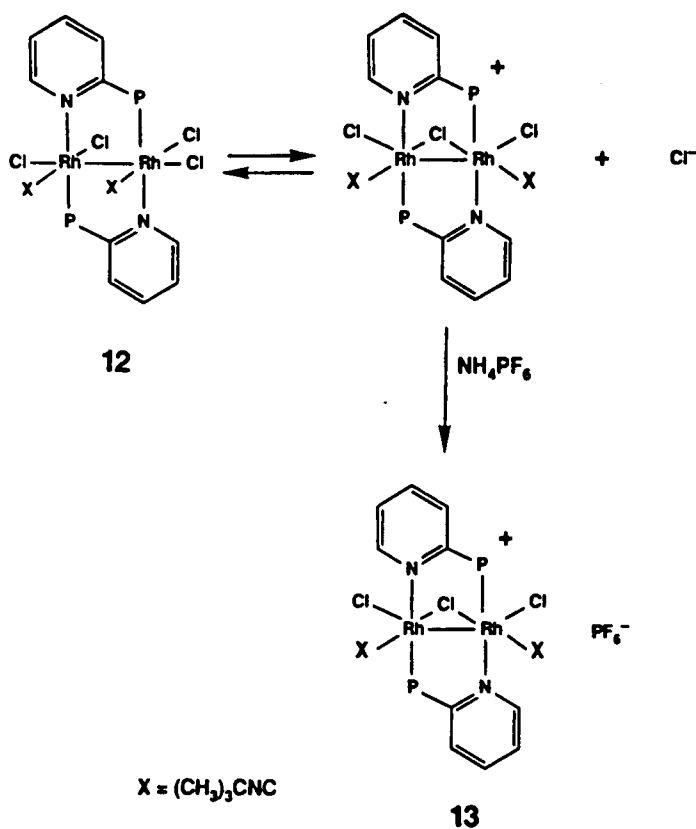


Figure 16. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of $\text{Rh}_2(\mu\text{-dppp})_2(\text{t-BuNC})_2\text{Cl}_4$, 12.

formulated as $[\text{Rh}_2(\mu\text{-dppp})_2\text{Cl}_2(\mu\text{-Cl})(\text{t-BuNC})_2](\text{PF}_6)$, 13, and its formation is summarized below.



The tendency of 12 to dissociate might be related to the short Rh-Rh bond distance and subsequent steric interactions resulting from the proximity of the t-BuNC ligands. This interaction can be reduced by twisting the dppp ligands such that when viewing 12 down the Rh-Rh bond axis the groups around the two rhodium atoms are in a slightly staggered conformation similar to that observed for 5 and 7. Further reduction of this interaction can be achieved through dissociation to form the chloro-bridged dirhodium cation. In the cation, the two planes containing the bound isocyanide carbons and the P-Rh-N axes are tilted so that they intersect at the

bridging Cl rather than being in an approximate parallel orientation. Thus, formation of the cation should allow the t -BuNC ligands to be further tilted away from each other resulting in a less sterically hindered species. The extent of dissociation of 12 is apparently small due to the coordinating ability of Cl^- and the nonionizing power of CH_2Cl_2 . Thus, a stoichiometric amount of the chloro-bridged dirhodium cation is not obtained until the Cl^- is precipitated with NH_4^+ and replaced with the noncoordinating anion PF_6^- .

The results of Chapters II and III clearly indicate that the tendency of dirhodium complexes to undergo the formation or cleavage of metal-metal bonds during chemical and electrochemical processes depends, in part, on structural constraints such as the ability of the bridging ligands to accommodate the required metal-metal distances. However, electronic properties of the ligands, such as σ and π acceptor ability, also play major roles in determining whether chemical or electrochemically-generated dirhodium products will exist with or without metal-metal bonds. The disposition of the transoid bridging ligands also affects the stability and nature of the product obtained from the chemical and electrochemical reactions.

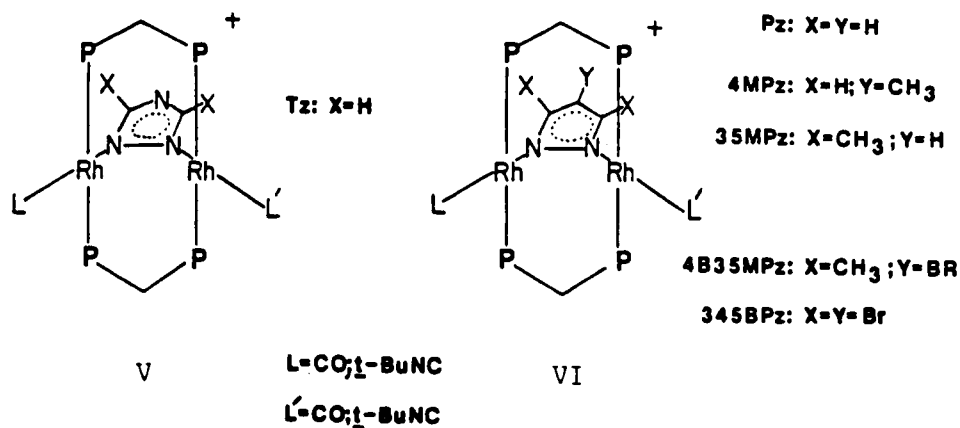
CHAPTER V

CHEMICAL AND ELECTROCHEMICAL BEHAVIOR OF (DPPM)₂- BRIDGED DIRHODIUM A-FRAME COMPLEXES CONTAINING A VARIETY OF SUBSTITUTED PYRAZOLATES AT THE BRIDGEHEAD POSITION

Most of the work on dinuclear A-frame complexes has centered on small molecules or single atoms at the bridgehead position. The incorporation of an aromatic compound into the apex position leads to the possibility of electron delocalization between the metal centers and the apex ligand. This delocalization may increase the versatility of the dinuclear unit as an electron-transport system, and increase the stability of different overall oxidation states of the dinuclear unit. Since no literature on dinuclear rhodium A-frame complexes containing aromatic heterocyclic ligands at the apex position has been reported, the study of dinuclear rhodium complexes containing triazolate and a variety of pyrazolates at the bridgehead position was undertaken.

These complexes include dirhodium(I) complexes that contain pyrazolate (Pz), 4-methylpyrazolate (4MPz), 3,5-dimethylpyrazolate (35MPz), 4-bromo-3,5-dimethylpyrazolate (4B35MPz), 3,4,5-tribromopyrazolate (345Bpz), and triazolate (Tz) as the apex ligand and terminal carbonyl and *t*-butylisocyanide ligands as illustrated by V and VI.

In the midst of the preparation of these complexes, a paper by L.A. Oro et al.³¹ appeared which contained the synthesis of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Z})]^+$ (Z=Pz, 3-methylpyrazolate, 35MPz,



4-bromopyrazolate), and the iodination products. Also published were the crystal structures of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-35MPz})](\text{ClO}_4)$ and $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{I}_2(\mu\text{-35MPz})](\text{ClO}_4)$. C. Janke⁸¹ demonstrated that complexes 18-21 undergo oxidative-addition reactions with Br_2 , Cl_2 and I_2 . The iodination products led to simple oxidative-addition reactions with the formation of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{I}_2(\mu\text{-Z})](\text{PF}_6)$ ($\text{Z}=\text{Pz}, 4\text{MPz}, 35\text{MPz}$).

In the case of Br_2 and Cl_2 , the oxidative-addition reactions have been shown to halogenate the four position of the Pz and 35MPz ligands in 18 and 19, as well as the rhodium atoms. This is not the case for 20 due to the methyl substituent in the four position of the pyrazolate ring blocking an attack by Cl_2 or Br_2 .

Addition of one equivalent $\bar{t}$ -BuNC to complexes 18-21 leads to the formation of 30-33 that contain one CO and one $\bar{t}$ -BuNC ligand on separate rhodium atoms. The structures of these mixed terminal- Π ligand dinuclear complexes are given by Structures V & VI where $\text{L}=\text{CO}$

and $L' = \underline{t}\text{-BuNC}$. The CO stretching frequencies for the mixed-ligand complexes occur between $1960\text{--}1980\text{ cm}^{-1}$, and the NC stretching frequencies of $\underline{t}\text{-BuNC}$ occur between $2122\text{--}2133\text{ cm}^{-1}$ (Table II). The IR spectra also reveal bands at $839(\text{s})$ and $557(\text{m})\text{ cm}^{-1}$ due to the presence of PF_6^- . The $^{31}\text{P}(\text{H})$ NMR spectrum of 30 is shown in Figure 17 and reveals an asymmetrical pattern which is representative of the $^{31}\text{P}(\text{H})$ NMR spectra of 30–33. The asymmetrical $^{31}\text{P}(\text{H})$ NMR pattern observed for 30–33 arises from an AA'BB'XY spin system. Addition of two equivalents of $\underline{t}\text{-BuNC}$ to complexes 18–23 results in the displacement of both carbonyl ligands, generating complexes 24–29 with structures shown by V and VI in which $L = L' = \underline{t}\text{-BuNC}$. The infrared spectra of the diisocyanide complexes exhibit CN stretching frequencies between 2060 and 2125 cm^{-1} (Table II). The $^{31}\text{P}(\text{H})$ NMR spectra of the diisocyanides exhibit the symmetrical second-order AA'A''A'''XX' pattern that is characteristic of symmetrical dinuclear rhodium complexes containing trans-bridging dppm ligands.¹⁷ The coupling constant, $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, for complexes 24–29 has a value of approximately 141 Hz , 13 Hz higher than those of the corresponding dicarbonyl complexes. The exact values of the coupling constants and chemical shifts for the diisocyanide complexes are given in Table III. The IR and $^{31}\text{P}(\text{H})$ NMR data for 23 are also shown in Tables II and III.

The analogous dpam and dapm compounds of 18–23 & 24–29 have been prepared by J. Burn and J. DePriest.⁸⁶ The crystal structure of $[\text{Rh}_2(\mu\text{-dpam})_2(\text{CO})_2(\mu\text{-35MPz})](\text{PF}_6)$ has been determined,⁸⁴ and is analogous to the crystal structure of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-35MPz})]$

TABLE II

IR DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{L})(\text{L}')(\mu\text{-Z})](\text{PF}_6)$

Z	L	L'	Compound number	$\nu\text{CO}, \text{cm}^{-1}$	$\nu\text{CN}, \text{cm}^{-1}$
345BPz	CO	CO	23	1992(s) 1975(m)	
Pz	CO	$\underline{t}$ -BuNC	30	1960(s)	2122(s)
4MPz	CO	$\underline{t}$ -BuNC	31	1972(s)	2122(s)
35MPz	CO	$\underline{t}$ -BuNC	32	1975(s)	2133(s)
Tz	CO	$\underline{t}$ -BuNC	33	1979(s)	2129(s)
Pz	$\underline{t}$ -BuNC	$\underline{t}$ -BuNC	24		2118(s) 2066(sh)
4MPz	$\underline{t}$ -BuNC	$\underline{t}$ -BuNC	25		2120(s) 2065(sh)
35MPz	$\underline{t}$ -BuNC	$\underline{t}$ -BuNC	26		2110(s) 2096(sh)
4B35MPz	$\underline{t}$ -BuNC	$\underline{t}$ -BuNC	28		2106(s) 2070(sh)
345BPz	$\underline{t}$ -BuNC	$\underline{t}$ -BuNC	29		2114(s) 2070(sh)
Tz	$\underline{t}$ -BuNC	$\underline{t}$ -BuNC	27		2124(s) 2064(sh)

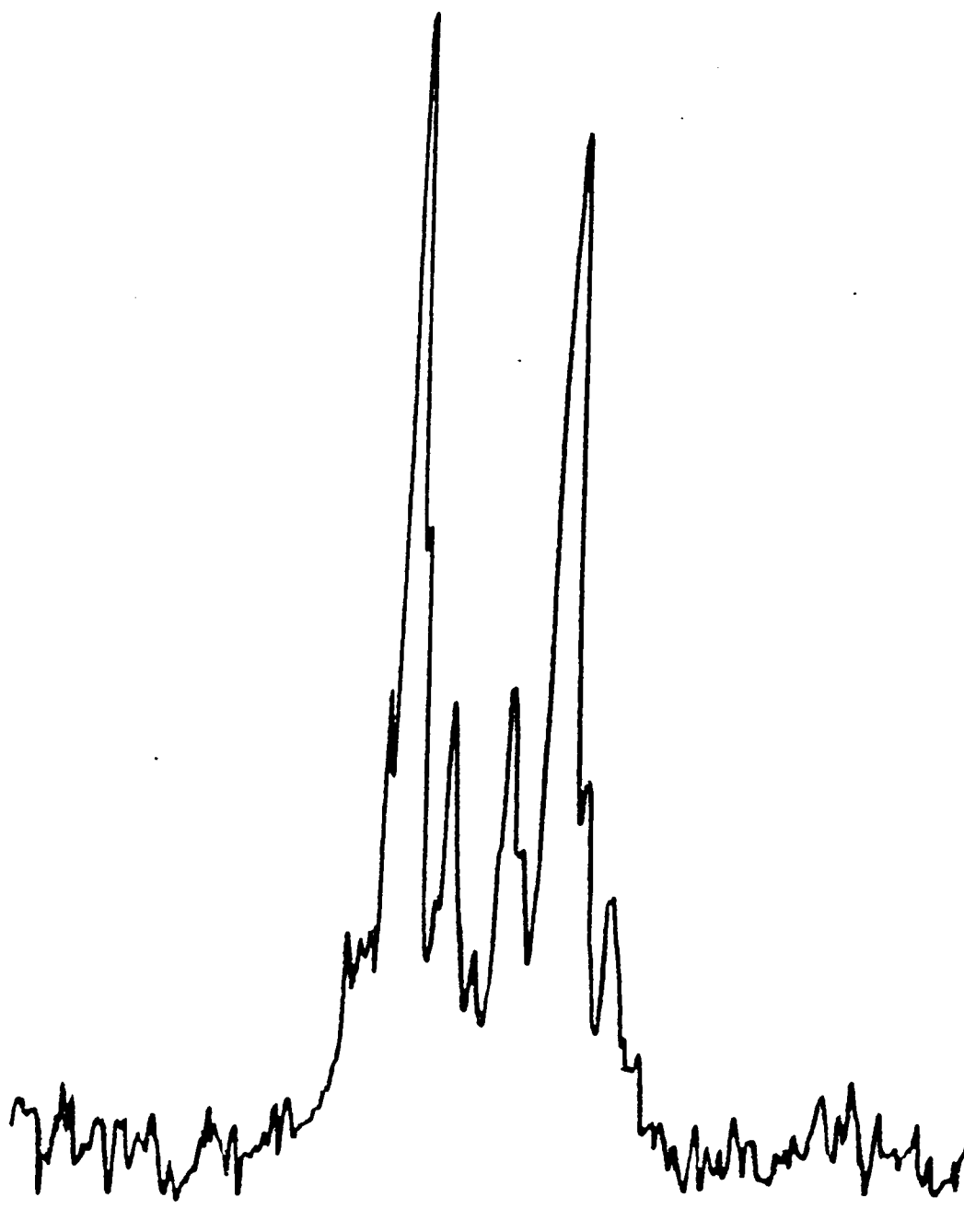


Figure 17. $^{31}\text{P}(\text{H})$ NMR spectrum of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})(t\text{-BuNC})(\mu\text{-Pz})](\text{PF}_6)$, 30.

TABLE III

$^{31}\text{P(H)}$ NMR DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{L})(\text{L}')(\mu\text{-Z})](\text{PF}_6)$

Z	L	L'	Compound number	δ , ppm	Coupling constant ^a
345BPz	CO	CO	23	20.6	126.9
Pz	<u>t</u> -BuNC	<u>t</u> -BuNC	24	22.7	141.6
4MPz	<u>t</u> -BuNC	<u>t</u> -BuNC	25	22.4	144.0
35MPz	<u>t</u> -BuNC	<u>t</u> -BuNC	26	20.3	139.2
4B35MPz	<u>t</u> -BuNC	<u>t</u> -BuNC	28	19.8	139.2
345BPz	<u>t</u> -BuNC	<u>t</u> -BuNC	29	18.0	139.2
Tz	<u>t</u> -BuNC	<u>t</u> -BuNC	27	21.7	139.2
^a $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, Hz					

(ClO₄) obtained by Oro et al.³¹ One notable difference between the two structures is the Rh-Rh separation of 3.060 and 3.220 Å for the dppm and dpam complexes, respectively. This difference is a direct effect of the larger bite size of the diarsine ligand compared to the diphosphine ligand, which leads to the larger Rh-Rh bond distance for the diarsine complex.

A. Spectroscopic Data of Dirhodium(I) A-Frames Containing dppm as the Transoid Bridging Ligand

The UV-Vis data show some interesting trends when the carbonyl ligands of the complexes [Rh₂(μ-dppm)₂(CO)₂(μ-Z)](PF₆) (Z = Pz, 4MPz, 35MPz, 4Br35MPz, Tz) are substituted with t-butylisocyanide ligands (Table IV), and when dppm is replaced by dapm and dpam for the dicarbonyl and diisocyanide complexes.

First, a discussion of the molecular orbital diagram for these pyrazolate complexes will be presented. The derivation of the molecular orbital diagram is essential in understanding the observed trends in the lowest-energy electronic transition. The molecular orbital approach described by D.M. and R. Hoffmann²¹ was adopted. For A-frame complexes, the orientation of the ten d-orbitals is shown below with the actual ordering of the eight lower orbitals depending on the angle θ, the metal-metal separation, and the apex ligand.

Also shown are the two uppermost d-orbitals which are directed in a σ fashion for interaction with the apex ligand, and are therefore devoid of electrons.

TABLE IV

LOWEST ENERGY UV-VIS TRANSITION FOR
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{L})(\text{L}')(\mu\text{-Z})](\text{PF}_6)$ COMPLEXES

Z	L-L'-CO λ , nm	L'-CO L-t-BuNC λ , nm	L-L'- t-BuNC λ , nm
Pz	492	505	514
4MPz	493	506	514
35MPz	484	496	505
4B35MPz	492		505
345BPz	480		492
Tz	487	493	505

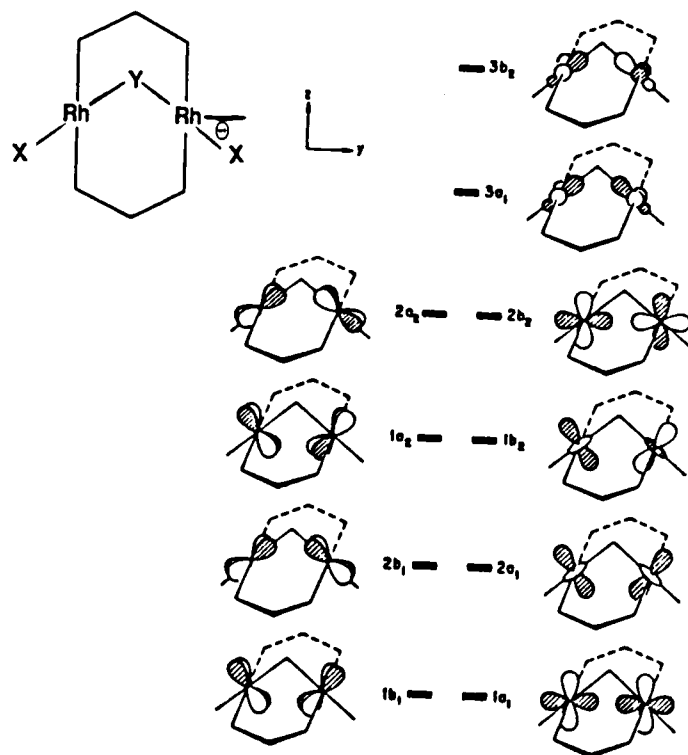


Figure 18 shows the orbital interaction of the pyrazolate ion with the $\text{Rh}_2(\mu\text{-dppm})_2\text{X}_2$ (X=terminal ligand) fragment. The pyrazolate's filled a_1 and b_2 σ orbitals interact with the empty $3a_1$ and $3b_2$ metal orbitals, respectively. The pyrazolate's a_1 and b_2 σ orbitals also interact with the filled $1a_1$ and $2b_2$ metal π orbitals. The filled pyrazolate's a_2 and b_1 π orbitals interact with the filled $2a_2$ and $2b_1$ metal π orbitals. Since M.O. energies have not been calculated, the exact ordering and the extent of interaction between the metal fragment and the pyrazolate orbitals can not be determined. However, it is believed that the antibonding combination of the filled $2a_2$ metal and the filled a_2 pyrazolate

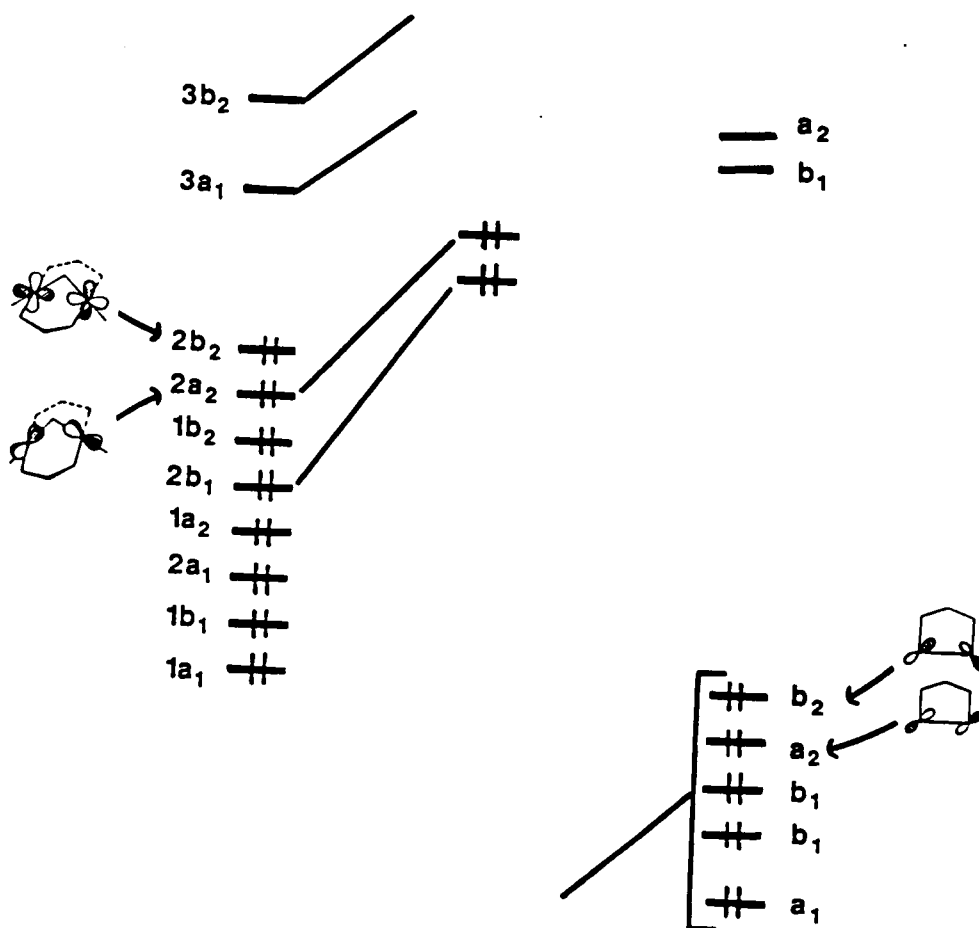


Figure 18. A MO diagram showing the orbital interaction between pyrazolate and the $[\text{Rh}_2(\mu\text{-dppm})_2\text{X}_2]^{2+}$ fragment.

orbitals becomes the HOMO of the pyrazolate-Rh₂ A-frame complex. Another combination that could give rise to the HOMO is the antibonding combination resulting from the interaction of the filled pyrazolate σ b₂ and the filled 2b₂ metal orbitals. In either case, the HOMO is metal-based and antibonding with respect to Rh-Rh interaction.

When the metal fragment contains terminal ligands with π - acceptor orbitals, like CO or CNR, which are pertinent to the complexes being investigated, four more orbitals appear in the molecular orbital diagram. These four orbitals of a₁, a₂, b₁, and b₂ symmetry have been determined to lie in energy between the 3a₁ and 3b₂ orbitals of the metal fragment.²¹ These four orbitals are the antibonding combination arising from the interaction between metal d π orbitals and the π^* orbitals of the π -acceptor terminal ligands, and are primarily ligand-based. Since these are low-lying orbitals, one becomes the LUMO of the dinuclear complex.

The UV-Vis data given in Table IV for these dirhodium complexes show that as the carbonyl ligands are replaced sequentially with *t*-BuNC, the lowest-energy transition shifts to lower energy. Since CO is considered to be a better π -acid ligand compared to isocyanide, the dinuclear rhodium complexes containing carbonyl ligands result in a stronger interaction between the carbonyl π^* orbitals and metal d π orbitals.

Figure 19 shows a comparison of the interaction between the π^* orbitals of the carbonyl and isocyanide ligands with the HOMO orbital derived from the Rh₂(μ -dppm)₂(μ -Pz)⁺ fragment. The

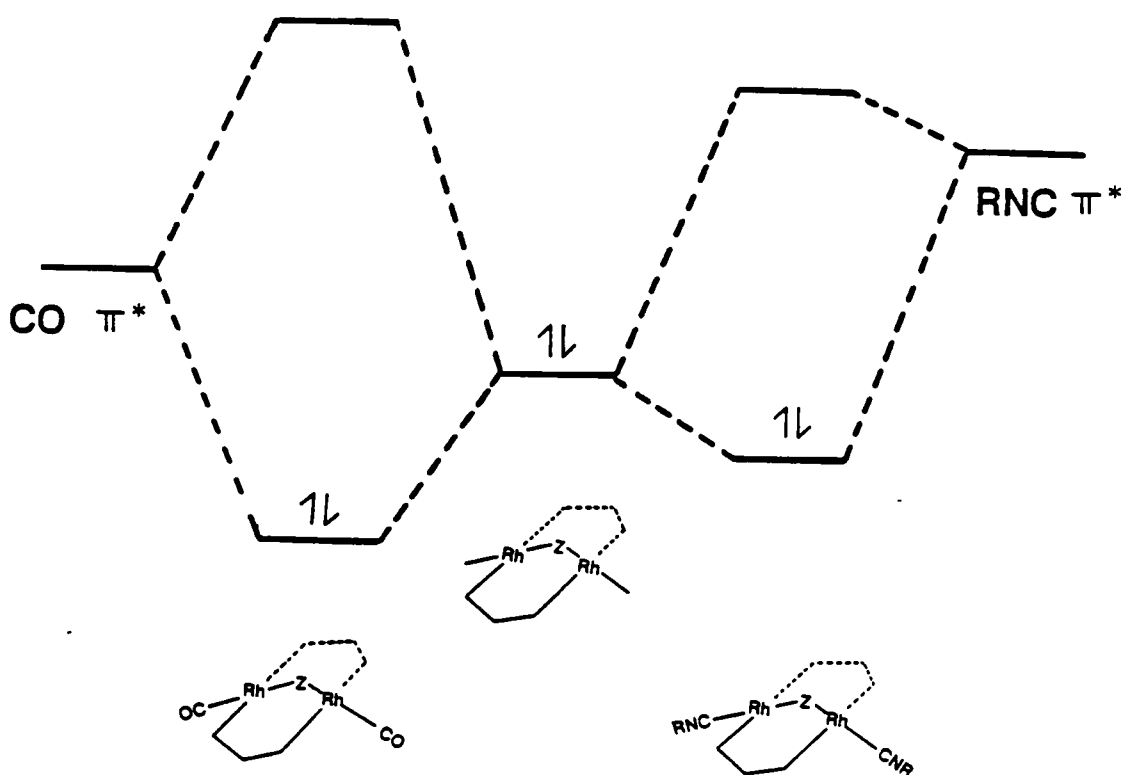
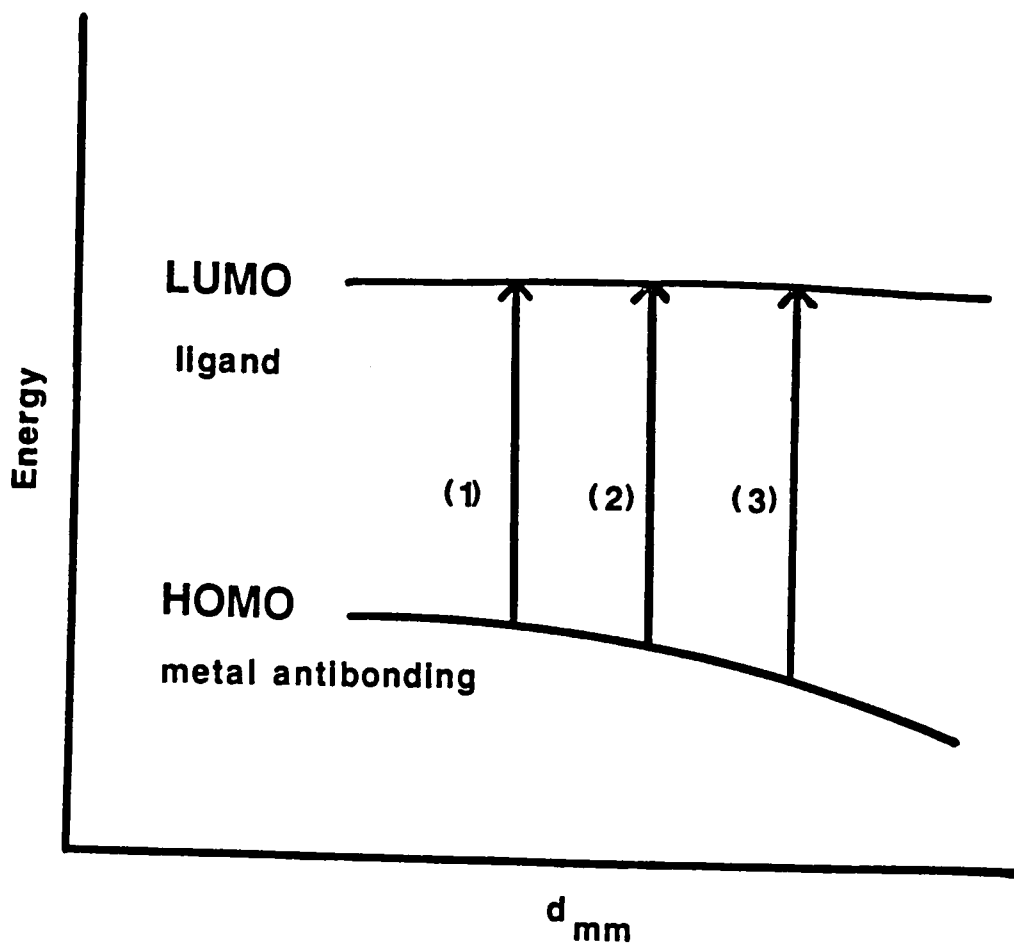


Figure 19. Simple qualitative MO diagram showing the effect of CO versus *t*-BuNC on the HOMO for pyrazolate-bridged dirhodium complexes.

interaction between the terminal ligands π^* orbital and the metal d-orbital perturbs the HOMO orbital by an amount which depends on the strength of this interaction. As the interaction increases in strength, the HOMO is lowered and the anti-bonding combination is raised in energy. The stronger interaction between the CO π^* orbital and the metal d-orbital results in the lowest-energy electronic transition being shifted to higher energy for the dicarbonyl complexes versus the diisocyanide complexes.

Further UV-Vis trends are observed from the data obtained from the analogous dppm, dapm,⁸⁶ and dpam⁸⁶ complexes. These data reveal that the lowest-energy electronic transition shifts to higher energy in the analogous dicarbonyl and diisocyanide complexes as the transoid-bridging ligand is changed in the order dppm < dapm < dpam. Replacement of a phosphorus donor atom with arsenic increases the Rh-Rh separation due to the larger bite size of dpam. This was earlier confirmed by the structural analysis of $\text{Rh}_2(\mu\text{-EE})_2(\text{CO})_2(\mu\text{-35MPz})]^+$ (EE=dppm,³¹dpam⁸⁶) which gave a Rh-Rh bond length for the dpam complex of 3.22 Å versus 3.06 Å for the dppm complex.

From the molecular orbital description, the HOMO is metal-based and is antibonding with respect to metal-metal interaction. A relative-energy diagram of the HOMO and LUMO as a function of the metal-metal separation is shown in Figure 20. As the metal-metal separation increases, the HOMO is stabilized due to its antibonding nature. A shift in the HOMO to LUMO electronic transition to higher energy as the metal-metal separation increases is also shown in the diagram. This model fits the observed trend that as the phosphorus



Transition	Complex	d_{mm} (Å)
(1)	$E=E'=P$	3.060
(2)	$E=P; E'=As$	(3.140)
(3)	$E=E'=As$	3.220

Figure 20. Variation of HOMO-LUMO separation versus Rh-Rh distance for $[Rh_2(\mu-EE')_2(CO)_2(\mu-35MPz)](PF_6)$ as EE' is changed from dppm to dapm to dpam. The metal-metal distance for the dapm complex is approximated by taking the mean distances of the dppm³¹ and dapm⁸⁴ complexes.

donor atoms are replaced with arsenic, the lowest-energy UV-Vis electronic transition shifts to higher energy or shorter wavelengths. This is a direct result of the larger metal-metal separation imposed by the larger bite sizes of the arsenic-containing ligands.

Although the orbital energies in the molecular orbital diagram have not yet been calculated, the data presented from the UV-Vis spectra are consistent with the proposed molecular orbital diagram.

B. Oxidative Addition of Some Pyrazolate Complexes Containing Terminal t -BuNC Ligands

Oxidative addition of 24-27 with one equivalent of I_2 and 24-27 and 29 with one equivalent of Br_2 generates crystalline brown and orange solids, respectively.

The iodination and bromination products, 44-52, exhibit terminal CN bands at approximately 2170 cm^{-1} (Table V), and PF_6^- bands at 839 and 557 cm^{-1} in the IR spectra. The higher CN stretching frequency of approximately 50 cm^{-1} from the corresponding parent compound results from an increased oxidation state of the rhodium atom from Rh(I) to Rh(II). The higher oxidation state of the rhodium atoms decreases the amount of Rh d $\pi \rightarrow$ C π^* back-bonding. The decrease in electron density in the carbon π^* orbitals of the isocyanide ligands results in the observed higher stretching frequencies of the CN bands in the IR spectra. The $^{31}P(H)$ NMR spectra of compounds 44-52 exhibit the symmetrical AA'A''A'''XX' pattern similar to the parent compounds.

TABLE V

IR AND $^{31}\text{P}\{\text{H}\}$ NMR DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{X}_2(\mu\text{-Z})](\text{PF}_6)$

Z	X	Compound number	IR	$^{31}\text{P}\{\text{H}\}$ NMR	
			$\nu_{\text{CN}}, \text{cm}^{-1}$	δ, ppm	coupling constant ^a
Pz	Cl	40	2176(s) 2164(sh)	4.3	92.8
4MPz	Cl	41	2176(s) 2165(sh)	4.2	90.3
35MPz	Cl	42	2176(s) 2172(sh)	10.7	92.7
Tz	Cl	43	2180(s) 2156(sh)	1.3	90.3
Pz	Br	44	2176(s) 2164(sh)	5.2	92.8
4MPz	Br	45	2176(s) 2168(sh)	5.2	92.8
35MPz	Br	46	2168(s) 2156(sh)	8.4	92.8
345BPz	Br	48	2165(s) 2155(sh)	7.9	92.8
Tz	Br	47	2172(s) 2166(sh)	1.9	90.3

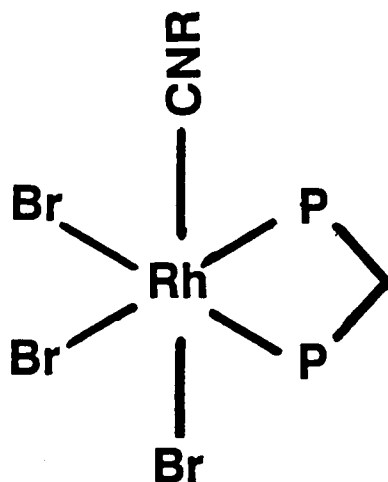
TABLE V (Continued)

Z	X	Compound number	IR	³¹ P(H) NMR	
			$\nu_{\text{CN}}, \text{cm}^{-1}$	δ, ppm	coupling constant ^a
Pz	I	49	2164(s) 2133(sh)	4.6	95.2
4MPz	I	50	2164(s)	4.6	95.3
35MPz	I	51	2156(s)	4.7	95.2
Tz	I	52	2156(s) 2172(s)	2.7	90.3
^a [$^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}$], Hz					

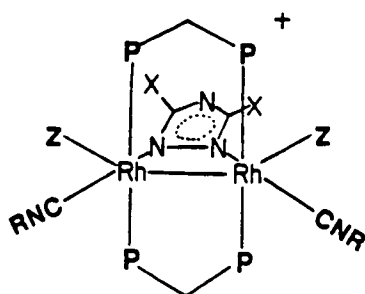
However, the values for the chemical shifts and [$^1J_{(Rh-P)} + ^xJ_{(Rh-P)}$] in the range of 2-11 ppm and 90-96 Hz, respectively are significantly reduced from those of the parent compounds (Table V).

When 24 is treated with excess Br_2 , the solution changes from purple-red to orange. The $^{31}P(H)$ NMR spectrum of the isolated product reveals a simple doublet at 14.0 ppm, and a coupling constant of 78.1 Hz. The IR spectrum indicates a terminal $\underline{t}$ -BuNC ligand with a CN stretching frequency of $2235(s) \text{ cm}^{-1}$, and the absence of PF_6^- . The simple doublet observed in the NMR spectrum demonstrates equivalent phosphorus atoms coupled to a single Rh atom ($I=1/2, 100\%$) with no long range coupling. The observed AX pattern is indicative of a monomer instead of a dinuclear species that gives rise to a $AA'A''A'''XX'$ spin system. The high CN stretching frequency of 2235 cm^{-1} , which is approximately 60 cm^{-1} higher than those observed in dinuclear Rh(II) complexes, indicates the formation of a Rh(III) species. These observations, when coupled with the analytical data that indicates the presence of three bromine atoms, led to the formulation of the isolated product as $Rh(dppm)(\underline{t}\text{-BuNC})Br_3$, whose structure is shown below. In this structure, each phosphorus atom is trans to a bromide ligand and cis to a $\underline{t}$ -BuNC and bromide ligand. This structure results in both phosphorus atoms being in equivalent chemical environments, and explains the observed doublet in the $^{31}P(H)$ NMR spectrum.

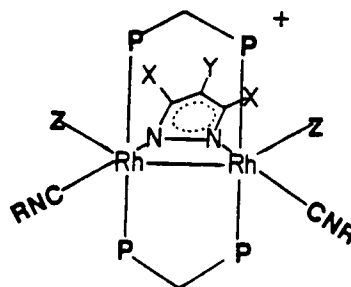
Treatment of 24 and 25 with Cl_2 results in oxidative-addition reactions generating yellow-orange solids. The IR and



$^{31}\text{P}\{\text{H}\}$ NMR data (Table V) of 40 and 42 are similar to the those of the bromo and iodo analogues. The proposed structures of all the halogenated pyrazolate and triazolate compounds, 44-52, are shown below.



Z = I, Br:
X = H



Z = I
X = Y = H
X = H; Y = CH₃
X = CH₃; Y = H

Z = Br:
X = Y = H
X = H; Y = CH₃
X = CH₃; Y = H
X = Y = Br

Z = Cl:
X = Y = H
X = H; Y = CH₃

R = C(CH₃)₃

Unlike the dicarbonyl complexes, 18 and 19, which when treated with Cl_2 and Br_2 are halogenated at the four position of the pyrazolate ring,⁸¹ the analogous diisocyanide complexes, 24 and 26, are not halogenated. In complexes 18 and 19, the four position of the pyrazolate ring is activated, possibly due to the enhanced back bonding ability of CO compared to t-BuNC . This allows CO to withdraw a larger amount of electron density from $\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-Pz})$, thus rendering the four position of the pyrazolate ring susceptible to attack by Cl_2 and Br_2 . Iodine does not attack the four position possibly due to its weaker oxidizing power.

C. Electrochemistry of Dinuclear Rhodium(I) Complexes
Containing Terminal CO and t-BuNC Ligands in CH_2Cl_2

The cyclic voltammograms of 18-21 obtained by C. Janke⁸¹ disclose a single two-electron quasi-reversible couple with $E_{1/2}$ values between +0.72 - +0.76 V. Further investigation of the electrochemical behavior of these complexes gave inconsistent cyclic voltammograms with different batches of CH_2Cl_2 . Freshly-distilled CH_2Cl_2 was then employed for all subsequent electrochemical studies on 18-23. A typical cyclic voltammogram of 18-20, 22 and 23 is illustrated by 18 in Figure 21A. The cyclic voltammogram of 18 in a CH_2Cl_2 solution containing 0.1 M TBAH reveals two apparent quasi-reversible couples with $E_{1/2}$ values of +0.763 and +1.31 V. Controlled-potential coulometry just past the first and second oxidation waves of 18-20, 22 and 23 indicates that each anodic wave corresponds to a one-electron transfer. If the potential is cycled initially in the negative direction, an irreversible reduction

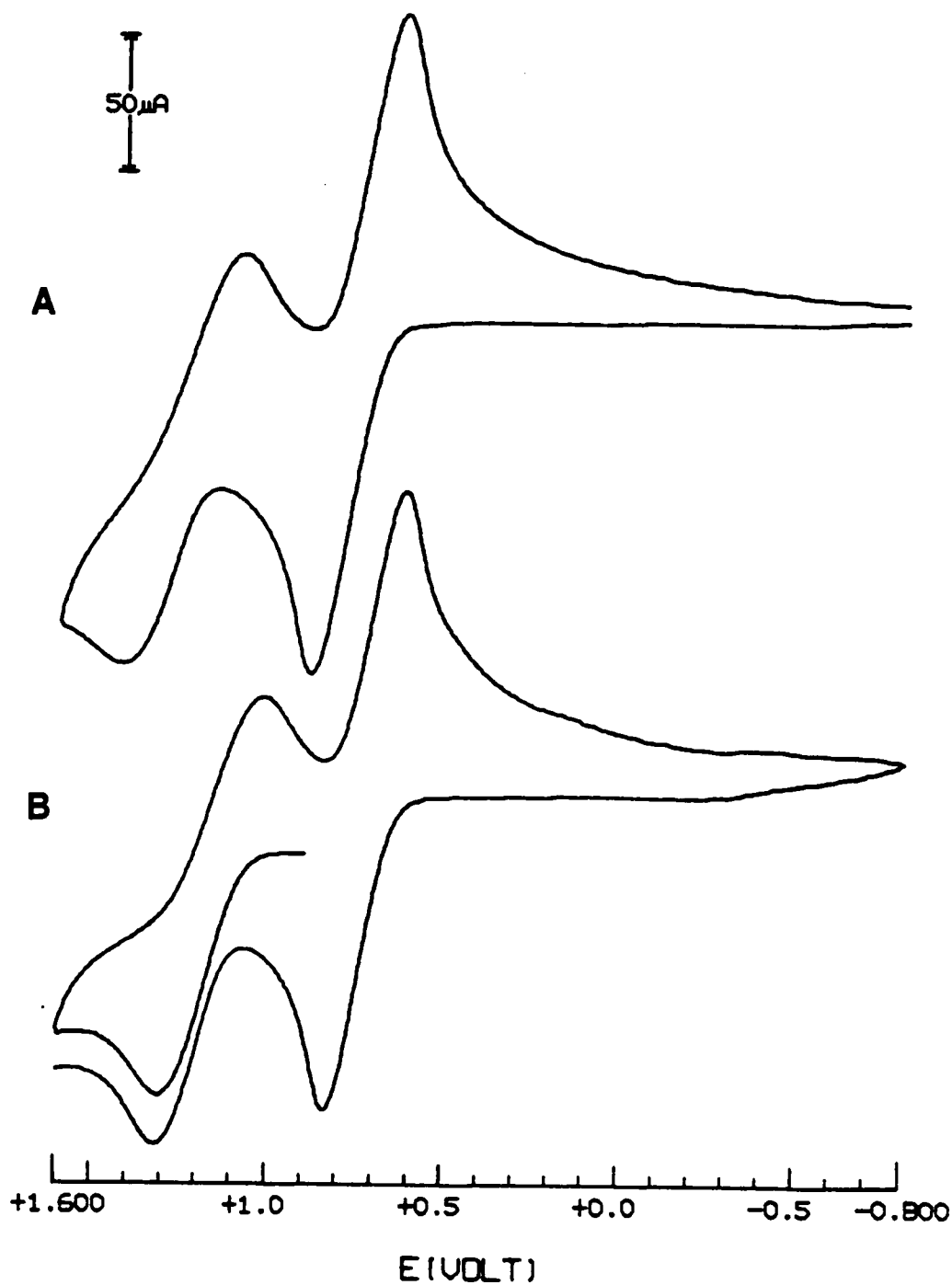


Figure 21. Cyclic voltammograms of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Pz})](\text{PF}_6)$, **18**, in $\text{CH}_2\text{Cl}_2/0.1$ M TBAH (A) before oxidation, and (B) after a one-electron oxidation.

wave at -1.899 V appears with the corresponding anodic waves at -1.925 and +0.571 V. The peak potentials corresponding to the second quasi-reversible couple and the irreversible cathodic wave for 18-20, 22 and 23 are given in Table VI.

The almost identical potential at which the cathodic and anodic waves occur for the electron-transfer process, approximately -1.8 V, possibly indicates adsorption of the electroactive species. Cycling the potential between -1.0 and -2.2 V in a CH_2Cl_2 solution containing 0.1 M TBAH and 20 reveals a decrease in the cathodic wave and a less-defined anodic response as the number of cycles increase. As the cycles are increased past approximately 30, the cathodic wave increases and a defined anodic wave returns. Transferring the rinsed electrode to a neat CH_2Cl_2 /TBAH solution results in the absence of any electrochemical activity. This rules out adsorption of the rhodium complex or any products generated by the possible reduction of the solvent.

In an attempt to determine the number of electrons transferred, compound 23 was chosen since its reduction wave occurs at the least-negative potentials compared to the other dicarbonyl species. Controlled-potential coulometry at -1.50 V in a CH_2Cl_2 solution containing 0.1 M TBAH and 23 results in a continual count of coulombs. The cyclic voltammogram after stopping the bulk electrolysis reveals two defined anodic waves at -0.195 and +0.879 V, and two cathodic waves at -0.413 and -1.7 V. Since oxidation of the reduced solution does not generate the parent compound, this

TABLE VI

ANODIC AND CATHODIC PEAK POTENTIALS FOR
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Z})](\text{PF}_6)$ COMPLEXES CORRESPONDING TO THE
 SECOND OXIDATION WAVE AND THE IRREVERSIBLE REDUCTION WAVE

Z	Compound number	Second oxidation wave ^a	Irreversible reduction wave ^{a, b}
		anodic/cathodic, V	cathodic/anodic, V
<u>Pz</u>	18		
CH ₂ Cl ₂		1.417/1.195	-1.899/-1.925, 0.571
CH ₃ CN			-1.625/ 0.425
<u>4MPz</u>	20		
CH ₂ Cl ₂		1.302/0.927	-2.050/-2.030,
			-0.190, 0.656
CH ₃ CN			-1.698/
<u>35MPz</u>	19		
CH ₂ Cl ₂		1.480/1.050	-1.963/-2.000
CH ₃ CN			-1.719/
<u>4B35MPz</u>	22		
CH ₂ Cl ₂		1.431/1.080	-1.775/-1.775, 0.617
CH ₃ CN			-1.657/-0.210
<u>345BPz</u>	23		
CH ₂ Cl ₂		1.448/1.150	-1.570/-0.069, 0.738
CH ₃ CN			-1.410/-0.245

^a Values recorded at a scan rate of 0.1 V/s

^b The cathodic wave in CH₂Cl₂ appears to involve the solvent.

indicates that 23 has undergone an irreversible structural change and/or chemical reaction. A continual count of coulombs possibly indicates that the rhodium complex is catalyzing the reduction of the solvent. There is insufficient data to determine a possible mechanism for the electron-transfer reaction; however, the reduction of the C-Cl bond of CH_2Cl_2 generating Cl^- and $\text{H}_2\text{ClC}\cdot$ can be eliminated.

If reduction of CH_2Cl_2 was occurring and generating free chloride ions, the cyclic voltammetric behavior of 18-20, 22 and 23 would be altered. The presence of chloride ions would result in an irreversible-oxidation process as the potential is cycled through positive potentials after sweeping through the reduction wave. However, the cyclic voltammograms reveal no alteration of the quasi-reversible or irreversible electron-transfer processes. It is believed that the rhodium complex is being initially reduced. Monitoring the CO stretching frequency by IR spectroelectrochemistry confirms the reduction of the dinuclear rhodium complex. At a rest potential of 0.0 V, the IR spectrum of 23 in a CH_2Cl_2 solution of 0.1 M TBAH reveals CO bands at 2008(s) and 1995(sh) cm^{-1} which indicate the presence of 23. Stepping the potential to -1.6 V leads to a decrease of about 29 cm^{-1} in the CO stretching frequencies to 1979(s) and 1968(m) cm^{-1} . These values are consistent with a reduction of Rh(I) to Rh(0).

The cyclic voltammetric data for the first one-electron couple, centered at approximately +0.718 V, for complexes 18-20, 22 and 23 are given in Table VII, and indicate the following: (1) the

TABLE VII

CYCLIC VOLTAMMETRIC DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Z})](\text{PF}_6)$ IN CH_2Cl_2

Z	v^a	E_{pa} , V	E_{pc} , V	ΔE , V	$E_{1/2}$, V	i_{pc}/i_{pa}
Pz, <u>18</u>	50	0.798	0.654	0.144	0.726	0.92
	100	0.816	0.644	0.172	0.730	0.92
	200	0.846	0.629	0.217	0.738	0.86
	300	0.869	0.615	0.254	0.742	0.80
	400	0.886	0.604	0.282	0.745	0.89
	500	0.914	0.587	0.327	0.750	0.75
35MPz, <u>19</u>	50	0.816	0.655	0.161	0.736	0.98
	100	0.830	0.641	0.189	0.736	0.98
	200	0.851	0.623	0.228	0.737	0.93
	300	0.871	0.605	0.266	0.738	0.91
	400	0.883	0.591	0.292	0.737	0.85
	500	0.889	0.583	0.306	0.737	0.87
4MPz, <u>20</u>	50	0.770	0.662	0.108	0.716	0.90
	100	0.777	0.658	0.119	0.718	0.90
	200	0.792	0.650	0.142	0.721	0.90
	300	0.800	0.644	0.156	0.722	0.90
	400	0.808	0.638	0.170	0.723	0.90
	500	0.810	0.630	0.180	0.720	0.90
4B35MPz, <u>22</u>	50	0.840	0.724	0.116	0.782	0.96
	100	0.845	0.715	0.130	0.780	0.96
	200	0.866	0.706	0.160	0.786	0.95
	300	0.872	0.700	0.172	0.786	0.95
	400	0.882	0.694	0.188	0.788	0.94
	500	0.890	0.688	0.202	0.789	0.94
345BPz, <u>23</u>	50	0.920	0.832	0.088	0.876	0.96
	100	0.923	0.831	0.092	0.877	0.97
	200	0.932	0.822	0.110	0.882	0.96
	300	0.935	0.816	0.119	0.876	0.97
	400	0.939	0.810	0.129	0.874	0.99
	500	0.940	0.804	0.136	0.872	0.98

^a Sweep rate in mV/s

potential separations, ΔE , between the anodic and cathodic peaks were in all cases greater than 60 mV and increased with scan rate; (2) the half-wave potentials, $E_{1/2}$, were invariant with scan rate, except for 18; (3) i_p values were proportional to the square root of the potential sweep rate; and (4) the ratios of the peak currents, i_{pc}/i_{pa} , were less than unity. Except for 18 and the current ratio, this behavior is consistent with a quasi-reversible one-electron couple.⁸⁷⁻⁸⁹

Controlled-potential electrolysis at potentials just past the quasi-reversible couple generates semi-stable dark-green paramagnetic species. Typical cyclic voltammograms before and after bulk electrolysis just past the first anodic wave are shown in Figure 21, illustrated by 18. These results indicate that 18 does not undergo structural rearrangement or a follow-up reaction after a one-electron oxidation. The only difference is in the peak potentials of the anodic and cathodic waves. A decrease of the quasi-reversible couple from an $E_{1/2}$ value of +0.763 to +0.729 V occurs after bulk oxidation. The anodic/cathodic responses corresponding to the second-electron process decrease after bulk oxidation from +1.42/+1.09 V to +1.33/+1.02 V.

The IR spectra of 66-70 exhibit two CO bands between 2033-2075 cm^{-1} (Table VIII). The increase in the CO stretching frequencies from those of 18-20, 22 and 23 results from a decrease in back-bonding between the rhodium Π and carbonyl Π^* orbitals due to an increase in the oxidation state of the rhodium atoms. The UV-Vis and NIR data of 66-70 are given in Table VIII.

TABLE VIII

SPECTROSCOPIC DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Z})](\text{PF}_6)_2$

Z	IR	UV-Vis	NIR
	$\nu\text{CO}, \text{cm}^{-1}$	$\lambda_{\text{max}}, \text{nm}(\epsilon)$	$\lambda_{\text{max}}, \text{nm}(\epsilon)$
Pz, <u>66</u>	2066(s)	660(1,300)	975(270)
	2045(s)	566(2,700)	
		519(3,300)	
		431(13,500)	
4MPz, <u>67</u>	2068(s)	665(840)	982(200)
	2040(s)	565(1,750)	
		520(2,100)	
		430(17,000)	
35MPz, <u>68</u>	2055(s)	693(750)	
	2033(s)	570(1,500)	
		519(2,060)	
		431(17,600)	
4B35MPz, <u>69</u>	2060(s)	685(1,100)	984(190)
	2035(s)	562(1,600)	
		491(3,100)	
		430(14,000)	
345BPz, <u>70</u>	2075(s)	678(1,300)	985(280)
	2049(s)	575(2,100)	
		525(2,030)	
		426(15,600)	

Since the two-electron oxidized complexes, 18-20, 22 and 23, cannot be isolated, IR spectroelectrochemistry has been employed to determine the CO stretching frequency as the potential is stepped past the second oxidation wave. A CH₂Cl₂ solution containing 0.1 M TBAH and 22 reveals an increase of 102 cm⁻¹ from 1998(s) and 1981(m) cm⁻¹ to 2100(s) and 2084(w) cm⁻¹ as the potential is stepped from a rest potential of 0.0 V to 1.4 V. Stepping the potential back to the rest potential, the CO bands at 1998(s) and 1981 cm⁻¹ reappear demonstrating the chemical reversibility of this system. The high-frequency CO bands at 2100 and 2084 cm⁻¹ are assigned to the formation of [Rh₂(μ-dppm)₂(CO)₂(μ-4B35MPz)](PF₆)₃, which exhibits CO bands 40 cm⁻¹ higher than 69.

The chemical reversibility is not unexpected since 18-20, 22 and 23 do not undergo a follow-up geometrical rearrangement or chemical reaction after a two-electron oxidation. As shown in Figure 22, the cyclic voltammogram of 20 before and after a two-electron bulk oxidation, in a CH₂Cl₂/TBAH solution, reveals no major differences. The only difference is a shift of the anodic and cathodic peak potentials to less positive potentials after bulk oxidation at +1.45 V. A shift in the E_{1/2} value for the first one-electron quasi-reversible couple from +0.751 to +0.709 V occurs after bulk oxidation. The E_{1/2} value corresponding to the second quasi-reversible one-electron couple shifts from +1.295 to +1.20 V after the two-electron bulk oxidation. The similarities of the cyclic voltammograms before and after bulk electrolysis signify the stability of 18-20, 22 and 23 following a two-electron oxidation.

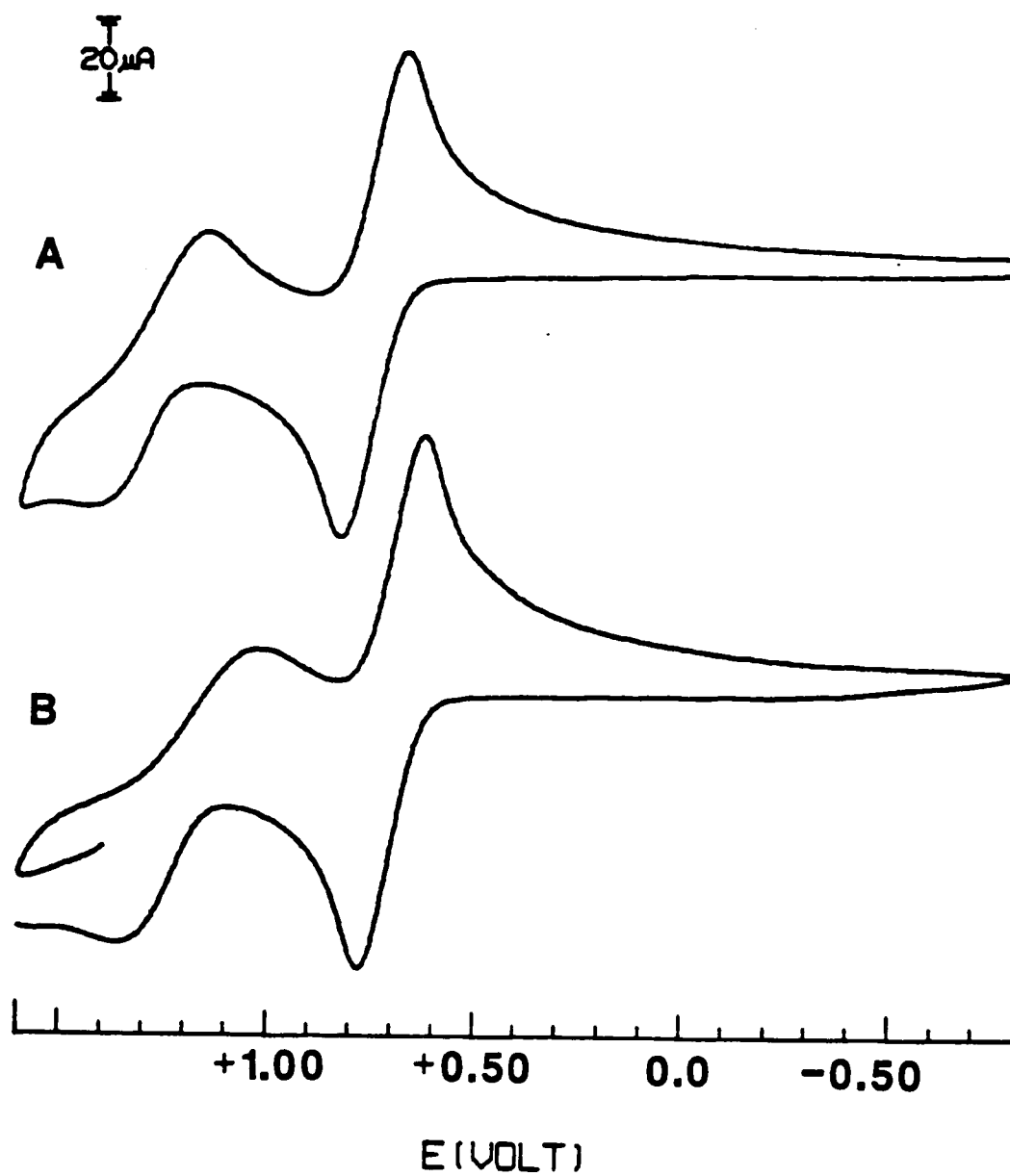


Figure 22. Cyclic voltammograms of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4MPz})](\text{PF}_6)$, 20, in $\text{CH}_2\text{Cl}_2/0.1$ M TBAH (A) before oxidation, and (B) after a two-electron oxidation.

The stability possibly originates from the delocalized π system involving the pyrazolate, rhodium and carbonyl orbitals. The delocalization of electron density results in the dinuclear rhodium(II) complexes not being as reactive following bulk oxidation in the absence of coordinating species.

The replacement of the carbonyl ligands with t -BuNC results in a decrease in the potential of the first and second one-electron couples. The observed decrease in potential is a direct effect of the weaker back-bonding ability of t -BuNC, which results in increased electron density on the rhodium atoms. This increased build-up of electron density at the metal centers corresponds to a decrease in the oxidation potential of the rhodium complexes. The increased electron density on the rhodium atom not only decreases the potential of the two oxidation waves, but may also contribute to the absence of a defined cathodic wave at approximately -2.0 V.

A typical cyclic voltammogram for 24-29 is illustrated in Figure 23A by that of 24. The cyclic voltammogram of 24 in a CH_2Cl_2 solution containing 0.1 M TBAH exhibits an apparent quasi-reversible couple with an $E_{1/2}$ value at +0.053 V, and an irreversible oxidation wave at +1.139 V with a cathodic response at +0.728 V. Table IX gives the peak potentials corresponding to the second-electron processes for complexes 24-29. Controlled-potential coulometry just past the first and second oxidation waves indicates that each anodic wave corresponds to a one-electron oxidation.

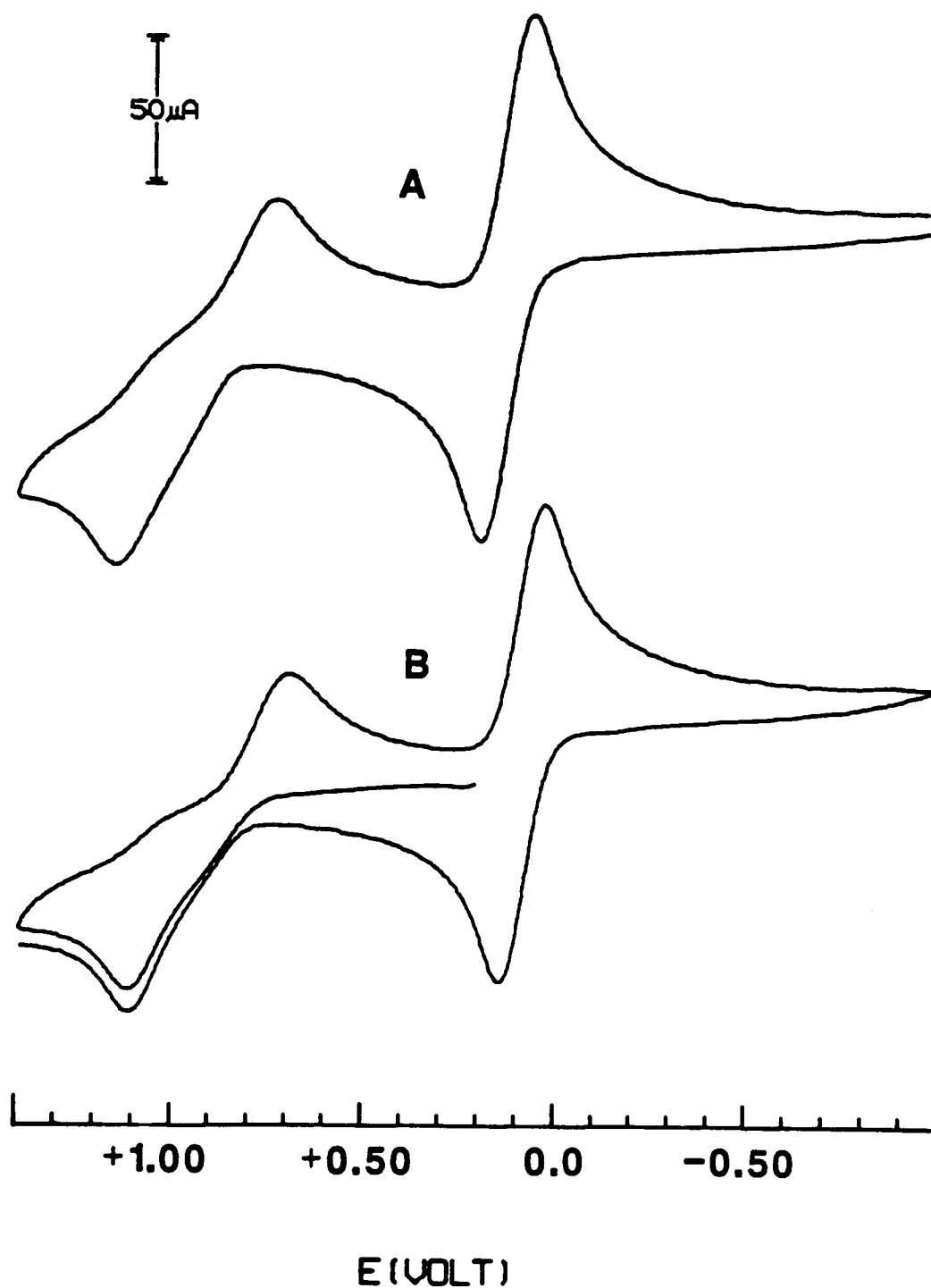


Figure 23. Cyclic voltammograms of 10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Pz})](\text{PF}_6)_2$, **24**, in $\text{CH}_2\text{Cl}_2/0.1$ M TBAH (A) before oxidation, and (B) after a one-electron oxidation.

TABLE IX

ANODIC AND CATHODIC PEAK POTENTIALS FOR
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Z})](\text{PF}_6)$ COMPLEXES
 CORRESPONDING TO THE SECOND-ELECTRON TRANSFER
 REACTION IN CH_2Cl_2

Z	<u>Second one-electron couple</u> ^a	
	anodic, V	cathodic, V
Pz, <u>24</u>	1.139	0.728
4MPz, <u>25</u>	1.124	0.686
35MPz, <u>26</u>	1.201	0.611
4B35MPz, <u>28</u>	1.175	0.698
345BPz, <u>29</u>	1.150	0.650
Tz, <u>27</u>	1.072	0.778

^a Values recorded at a scan rate of 0.1 V/s

The stability of complexes 24-29 after the removal of two electrons is indicated by similar cyclic voltammograms before and after bulk oxidation. The cyclic voltammogram of 26 in a CH_2Cl_2 solution containing 0.1 M TBAH reveals a quasi-reversible couple with an $E_{1/2}$ value of +0.069 V, and an irreversible oxidation at +1.160 V with the corresponding cathodic response at +0.683 V (Figure 24A). Bulk electrolysis at +1.2 V results in a two-electron transfer. The cyclic voltammogram of the resulting oxidized solution reveals an $E_{1/2}$ value of +0.050 V for the first one-electron couple, and cathodic and anodic potentials of +0.659 and +1.136 V, respectively, for the second-electron process (Figure 24B). The difference in the cyclic voltammograms before and after bulk oxidation is a slight shift to less-positive potentials of the anodic and cathodic responses.

Data for the first one-electron couple of 24-30 are given in Table X, and indicate the following: (1) the potential separations, ΔE , between the anodic and cathodic peaks were in all cases greater than 60 mV, and increased with scan rate; (2) the half-wave potentials, $E_{1/2}$, were invariant with scan rate; (3) i_p values were proportional to the square root of the potential sweep rate, and (4) the ratios of the peak currents, i_{pc}/i_{pa} , were approximately unity. This behavior is consistent with a one-electron quasi-reversible couple.⁸⁷⁻⁸⁹

The electrochemical data obtained for the removal of the first electron for the analogous dicarbonyl and diisocyanide dinuclear rhodium complexes containing dapm and dpam bridging

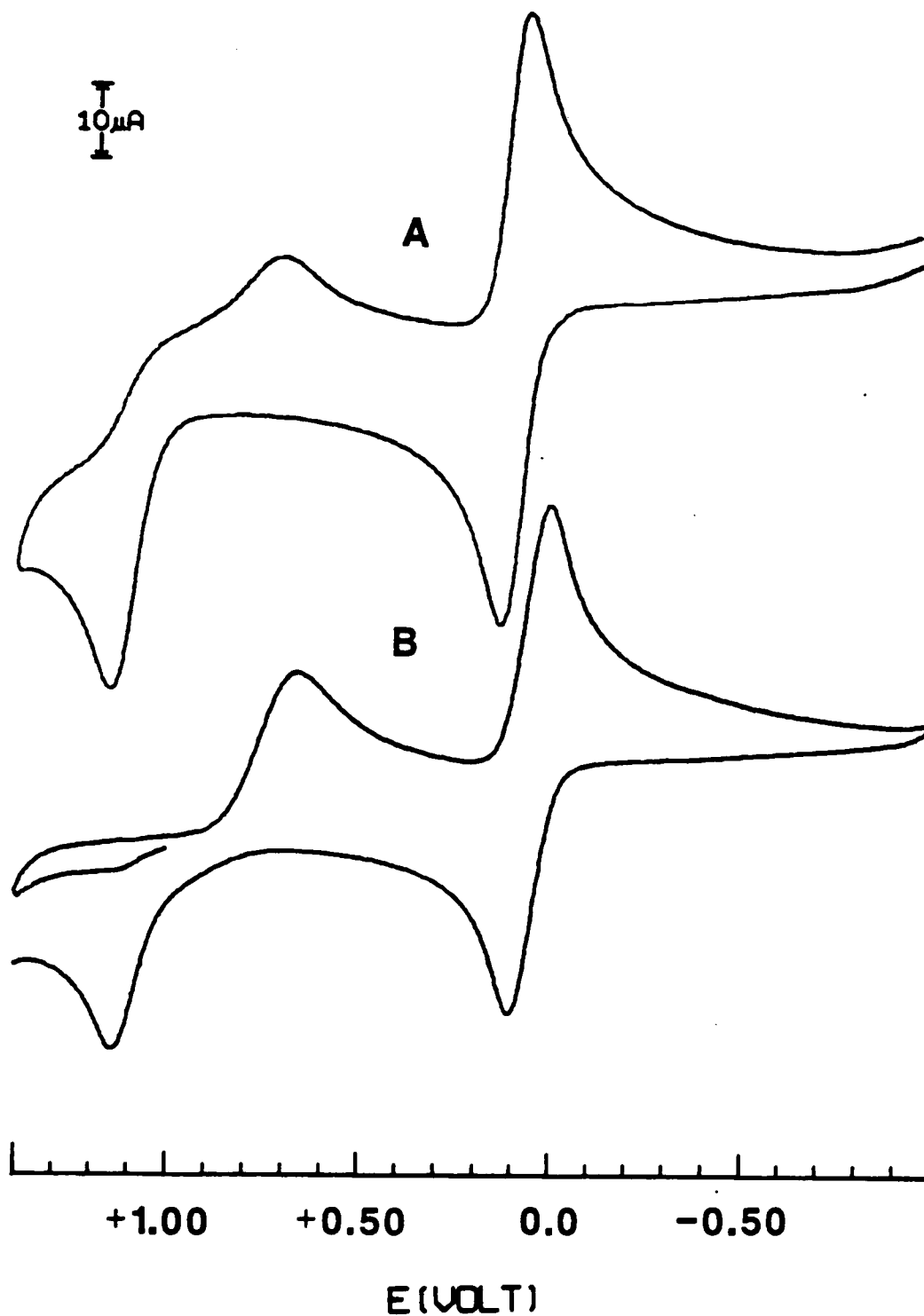


Figure 24. Cyclic voltammograms of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)$, 26, in $\text{CH}_2\text{Cl}_2/0.1$ M TBAH (A) before oxidation, and (B) after a two-electron oxidation.

TABLE X

CYCLIC VOLTAMMETRIC DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Z})](\text{PF}_6)$ IN CH_2Cl_2

Z	v^a	E_{pa} , V	E_{pc} , V	ΔE , V	$E_{1/2}$, V	i_{pc}/i_{pa}
Pz, <u>24</u>	50	0.122	-0.027	0.148	0.048	1.06
	100	0.139	-0.033	0.172	0.053	1.06
	200	0.160	-0.049	0.209	0.056	1.05
	300	0.176	-0.062	0.238	0.057	0.97
	400	0.184	-0.066	0.250	0.059	0.95
	500	0.194	-0.074	0.268	0.060	0.93
4MPz, <u>25</u>	50	0.133	-0.014	0.147	0.060	1.07
	100	0.143	-0.027	0.170	0.058	1.07
	200	0.156	-0.050	0.206	0.053	1.06
	300	0.169	-0.064	0.233	0.053	1.05
	400	0.182	-0.074	0.256	0.054	0.96
	500	0.187	-0.081	0.268	0.053	0.91
35MPz, <u>26</u>	50	0.116	-0.006	0.122	0.055	1.00
	100	0.119	-0.009	0.128	0.055	1.00
	200	0.132	-0.021	0.153	0.056	1.00
	300	0.141	-0.027	0.168	0.057	1.00
	400	0.147	-0.032	0.179	0.058	1.00
	500	0.154	-0.036	0.190	0.059	1.00
Tz, <u>27</u>	50	0.267	0.164	0.103	0.216	1.00
	100	0.286	0.169	0.117	0.228	1.00
	200	0.296	0.154	0.142	0.225	1.00
	300	0.303	0.147	0.156	0.225	1.00
	400	0.303	0.135	0.168	0.219	1.00
	500	0.315	0.128	0.187	0.222	1.00
4B35MPz, <u>28</u>	50	0.177	0.049	0.128	0.113	1.00
	100	0.188	0.043	0.145	0.116	1.00
	200	0.205	0.028	0.177	0.117	1.00
	300	0.220	0.013	0.207	0.117	1.00
	400	0.231	0.008	0.223	0.120	1.00
	500	0.235	0.006	0.229	0.121	1.00

TABLE X (Continued)

Z	v^a	E_{pa} , V	E_{pc} , V	ΔE , V	$E_{1/2}$, V	i_{pc}/i_{pa}
345BPz, <u>29</u>	50	0.295	0.154	0.141	0.225	1.00
	100	0.309	0.146	0.163	0.228	1.00
	200	0.329	0.141	0.188	0.235	1.00
	300	0.341	0.127	0.214	0.234	1.00
	400	0.356	0.117	0.266	0.237	0.98
	500	0.369	0.111	0.258	0.240	0.98

^a Scan rate in mV/s

ligands⁸⁶ are consistent with the proposed molecular orbital diagram referred to earlier (Figure 18, page 143). The data reveal that as the transoid-bridging ligand is changed from dppm to dpam, an increase in the anodic potential occurs with dapm being intermediate. This observation results from the increasing bite size of the bridging ligand as phosphorus is replaced with arsenic, which causes an increase in the Rh-Rh separation. As the metal-metal distance increases, the HOMO decreases in energy, thus requiring an increased potential for the removal of the first electron. However, comparing the electrochemical data for the removal of the second electron reveals an inverse trend. The potential required to remove the second electron increases in the order $\text{dpam} < \text{dapm} < \text{dppm}$.

As stated previously, the cyclic voltammograms of 24-29 exhibit two consecutive one-electron oxidations. Stable green paramagnetic species are generated via controlled-potential electrolysis at a potential between the quasi-reversible and irreversible couples. Typical cyclic voltammograms, in a $\text{CH}_2\text{Cl}_2/\text{TBAH}$ solution, before and after the removal of a single electron are shown for 24 in Figure 23, page 164. These voltammograms indicate that 24 does not undergo major structural rearrangement or follow-up reactions following the one-electron oxidation. The only difference is the position of the anodic and cathodic responses. The $E_{1/2}$ value for the quasi-reversible couple decreases from 0.093 to 0.075 V after bulk oxidation. The anodic potential for the removal of the second electron changes from +1.14 to +1.11 V, and the cathodic response changes from +0.701 to +0.698 V after bulk oxidation.

The paramagnetic complexes, 34-39, exhibit no $^{31}\text{P(H)}$ NMR spectra due to the rapid relaxation of the phosphorus nuclei imposed by the unpaired electron. Since the magnetic moment of an electron is about a thousand times larger than those of most nuclei, an unpaired electron can produce a high local magnetic field.^{90,91} The large magnetic moment, in conjunction with the short electron spin relaxation time, causes the local field to fluctuate and thus induces fast transitions between the nuclear spin states. The rapid relaxation of the nucleus makes observation of a nucleus by NMR spectroscopy almost impossible, especially when the unpaired electron is based near the nucleus under observation. Complexes 34-39 exhibit CN stretching frequencies in the IR spectrum between 2158-2176 cm^{-1} (Table XI), which is approximately 60 cm^{-1} higher than those of the parent compounds. A decrease in back-bonding into the carbons π^* orbitals of the isocyanide ligand results from a decrease in electron density on the rhodium atoms as the oxidation state is increased from Rh(I) to Rh(1.5). The absence of two separate CN bands indicates that the lone electron is delocalized between the two rhodium atoms. The UV-Vis data reveal a broad band at approximately 600 nm, and a sharper band between 421 and 429 nm (Table XI). The NIR spectra reveals two overlapping bands between 840 and 1000 nm; whereas the parent compounds do not absorb in the NIR region of the electromagnetic spectrum (Table XI).

The UV-Vis and NIR data for $[\text{Rh}_2(\mu\text{-EE}')_2(\text{t-BuNC})_2(\mu\text{-Z})](\text{PF}_6)_2$ (EE'-dppm, dapm, $^{86}\text{dpam}^{86}$; Z=4MPz, 4B35MPz, 345BPz) correlate with the observed electrochemical data for the removal of the second

TABLE XI

SPECTROSCOPIC DATA FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Z})](\text{PF}_6)_2$
COMPLEXES

Z	IR	UV-Vis	NIR
	$\nu_{\text{CN}}, \text{cm}^{-1}$	$\lambda_{\text{max}}, \text{nm}(\epsilon)$	$\lambda_{\text{max}}, \text{nm}(\epsilon)$
Pz, <u>34</u>	2172(s)	580(1,200)	845(750)
	2161(m)	427(32,000)	994(380)
4MPz, <u>35</u>	2172(s)	562(1,110)	849(630)
		427(26,000)	990(310)
35MPz, <u>36</u>	2168(s)	583(1,200)	862(850)
	2166(sh)	429(24,700)	996(370)
4B35MPz, <u>37</u>	2174(s)	580(1,400)	862(850)
	2156(m)	427(33,700)	994(300)
345BPz, <u>38</u>	2174(s)	604(1,300)	853(730)
	2158(sh)	422(19,000)	980(325)
Tz, <u>39</u>	2176(s)	575(1,900)	846(750)
	2171(sh)	421(29,000)	988(375)

electron. As noted earlier, the order of the potential energy for the removal of the second electron is $dppm > dapm > dpam$. The low-energy electronic transitions that occur in the UV-Vis and NIR region of the electromagnetic spectrum occur at lower energy in the order $dpam < dapm < dppm$. These data indicate that the separation between the HOMO and LUMO is smallest for the $dpam$ complexes, presumably a result of the HOMO being higher in energy, since the LUMO is ligand-based and should remain relatively constant. An effect of the HOMO being higher in energy for the $dpam$ complexes is a decrease in potential for the removal of the second electron as observed in the electrochemical data.

D. ESR Spectroscopy of Electrochemically-Generated Paramagnetic Complexes

The room-temperature solution ESR spectra of the paramagnetic cations, 34-39, show isotropic signals with no hyperfine coupling. The isotropic g values for 34-39 from the room-temperature solution spectra are all within 2.15 ± 0.01 with a line width of $46 \pm 1G$, and suggest that the partially-occupied orbital is essentially metal-based. The anisotropic g values of the polycrystalline samples at room-temperature are also consistent with the description of the odd-electron orbital as a metal-based orbital.

The frozen-solution of 38 in 4:1 CH_2Cl_2 /toluene at 77 K is green and its ESR spectrum is shown in Figure 25A. This spectrum closely resembles that recently reported for a similar mixed-valence dirhodium complex.²⁰ The frozen solution spectrum of 38 is

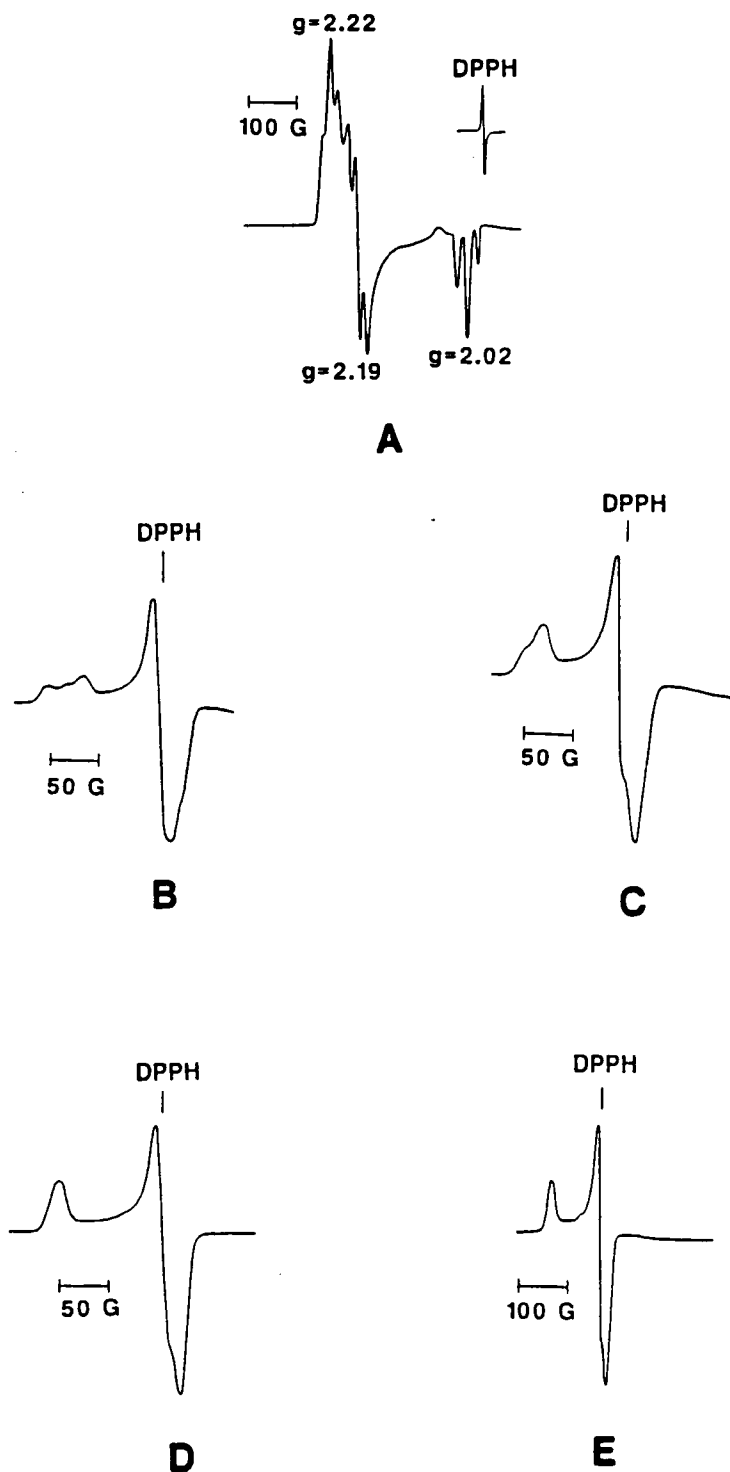


Figure 25. ESR spectra of 4:1 CH_2Cl_2 /toluene solutions at 77 K of $[\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-BuNC})_2(\mu\text{-Z})](\text{PF}_6)_2$; Z= (A) 345BPz, 38, (B) Pz, 34, (C) 4MPz, 35, (D) 35MPz, 36, and (E) 4B35MPz, 37.

interpreted as that of an orthorhombic system with observable components at g-values of 2.02, 2.19 and 2.22. These g-values are consistent with a metal-centered radical. The high-field component in the spectrum of 38 clearly shows hyperfine splitting into a triplet with $A = 20.05 \times 10^{-4} \text{ cm}^{-1}$. This splitting is attributed to spin-coupling to two equivalent rhodium nuclei ($^{103}\text{Rh}, 100\%, I=1/2$). These results present clear evidence that the unpaired electron spin is delocalized over two rhodium nuclei in equivalent environments. In the case of a similar dirhodium complex containing two transoid bis(diphenylphosphino)methane ligands, one of the ESR components occurs as a five-line pattern for which the splitting is attributed to hyperfine coupling to the four equivalent phosphorus atoms. In this previous report it was noted that an expected third ESR component was not observed and was presumed to be masked by the five-line multiplet. In the case of 38, a six-line multiplet is observed for one of the ESR components. A five-line pattern with $g = 2.19$ and exhibiting a hyperfine coupling of $21.00 \times 10^{-4} \text{ cm}^{-1}$ can be extracted from this multiplet leaving a single line at $g = 2.22$. As a result, this multiplet was interpreted as the superimposition of the component at $g = 2.19$ showing hyperfine splitting to the four equivalent phosphorus atoms, and the expected third component of the orthorhombic system at $g = 2.22$. The signal at $g = 2.19$ is associated with the Rh_2P_4 principal magnetic axis, and the signal at $g = 2.22$ is associated with the $\text{Rh}_2\text{N}_2\text{C}_2$ principal magnetic axis.

Unlike the behavior of the CH_2Cl_2 /toluene solution of 38, solutions of 34-37 in 4:1 CH_2Cl_2 /toluene change color from green to

red upon freezing at 77 K. The solution thermochromism is reversible; however, this thermochromic effect is not observed for the polycrystalline samples. The red frozen solutions of 34-37 exhibit ESR spectra (Figure 25) that are quite different from the frozen-solution spectrum of 38. The spectra of 34-37 are interpreted as those of anisotropic systems for which the high-field and intermediate-field components overlap. Because of this overlap the g values reported for these components, 2.00 and 1.99, are only approximate, but are essentially the same for the four complexes (Table XII). The low-field components for 34-37 occur at approximately $g = 2.06$ (Table XII). It should be noted that the nature and the g values of the ESR signals for 34-37 are significantly different from those observed for 38. This significant change in g -values, upon freezing the solutions at 77 K, suggests that for 34-37 the unpaired electron may no longer be metal-centered at 77 K.

The low-field ESR components of 34 and 35 show some splitting; however, the analogous signals for 36 and 37 are unsplit. If the unpaired electron is located on the ligand at 77 K, the splitting of the low-field signal for 34 and 35 might result from hyperfine splitting with the hydrogen atoms on the heterocyclic ring, particularly those in the 3- and 5- positions since the 3,5-substituted derivatives do not show similar splittings. Deuteriated pyrazole was synthesized in an attempt to further investigate the possibility that the unpaired electron is located on the pyrazolate ligand. Synthesis of d_4 -pyrazole gave the following mass spectrometric data: 23.6% 1,3,4,5- d_4 -pyrazole and 37% 1,3,4- d_3 and

TABLE XII

ESR DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Z})](\text{PF}_6)_2$

Z	High field	Intermediate field	Low field
	$g^a(\text{A})^b$	g^a	$g^a(\text{A})^b$
Pz, <u>34</u>	1.99 2.00	2.06	
4MPz, <u>35</u>	1.99 2.00	2.06	
35MPz, <u>36</u>	1.99 2.00	2.07	
4B35MPz, <u>37</u>	1.99 2.00	2.07	
345BPz, <u>38</u>	2.02(20.05 x 10 ⁻⁴)		2.19(21.0 x 10 ⁻⁴) 2.22

^a 4:1 CH₂Cl₂/toluene solutions at 77 K
^b A values in cm⁻¹

1,4,5-d₃-pyrazole. Although deuteration was not complete, the ESR spectrum was obtained for the deuteriated analogue of 34, 65. The frozen solution ESR spectrum of 65 shows a slight variation in the splitting of the low-field component in comparison to 34.

Variable-temperature ESR studies of analogous dapm and dpam⁸⁶ complexes indicate that the thermochromic effect is continuous, with one isomer developing as the other isomer disappears such that only the low-temperature form is present at 77 K.

If the unpaired electron at 77 K is localized on the pyrazolate ligand, such a configuration would arise from either a ligand-to-metal or metal-to-ligand charge transfer. A metal-to-ligand charge transfer would result in both rhodium atoms in an oxidation state of +2 and a dianionic pyrazolate ligand. On the other hand, a ligand-to-metal charge transfer will result in a neutral heterocyclic ligand with both rhodium atoms in a +1 oxidation state. In either case, the CN stretching frequency of the t-BuNC ligands can be probed to determine if a metal-to-ligand or ligand-to-metal charge transfer is occurring. If a ligand-to-metal charge transfer is occurring, the CN band should appear at a frequency similar to the dinuclear Rh(I) parent compound. For a metal-to-ligand charge transfer, the CN stretch should be higher than for the one-electron oxidized species or at approximately the CN stretch for the two-electron oxidized species. Since a stable dinuclear Rh(II) cation can not be isolated, an IR spectrum was obtained of the electrochemically generated $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})]^{3+}$ cation by in situ IR spectroelectrochemistry.

The cyclic voltammogram of 25 in a CH_2Cl_2 solution containing 0.1 M TBAH is shown in Figure 26, and demonstrates the effect of an increased IR drop resulting from the cell design used to obtain in situ IR spectra. Points where the potential was stepped for each IR spectrum are also designated in Figure 26. Figure 27 shows a potential difference IR spectrum of 25 for potentials of -0.4 V (Test 1) and +0.70 V (Test 2). The potential-difference IR spectrum indicates that 35 is generated when the potential is stepped to +0.60 V. The CN stretching frequencies at 2121 and 2171 cm^{-1} , indicated in Figure 27A, match those obtained for 25 and 35 from the nujol mulls. Stepping the potential to 1.5 V (Test 3) generates the dinuclear Rh(II) dimer. Figure 27B shows a potential-difference IR spectrum of 25 and the electrochemically-generated Rh(II) dimer. The CN stretching frequency obtained for the dinuclear Rh(II) species of 2189 cm^{-1} is 19 cm^{-1} higher than for 35. The increase in the CN stretching frequency as the potential is stepped from Test 1 to Test 3 results from a decrease in back-bonding between the metal and the isocyanide ligand as a result of an increase in oxidation state of the metal. Although the first oxidation is quasi-reversible and the second is irreversible, each species generated electrochemically is chemically reversible. This has been demonstrated by in situ IR data obtained by oxidizing 25 in two successive one-electron oxidations followed by two successive one-electron reductions. The chemical reversibility is not surprising since a two-electron oxidation of 24-29 does not result in any major structural change or a follow-up chemical reaction.

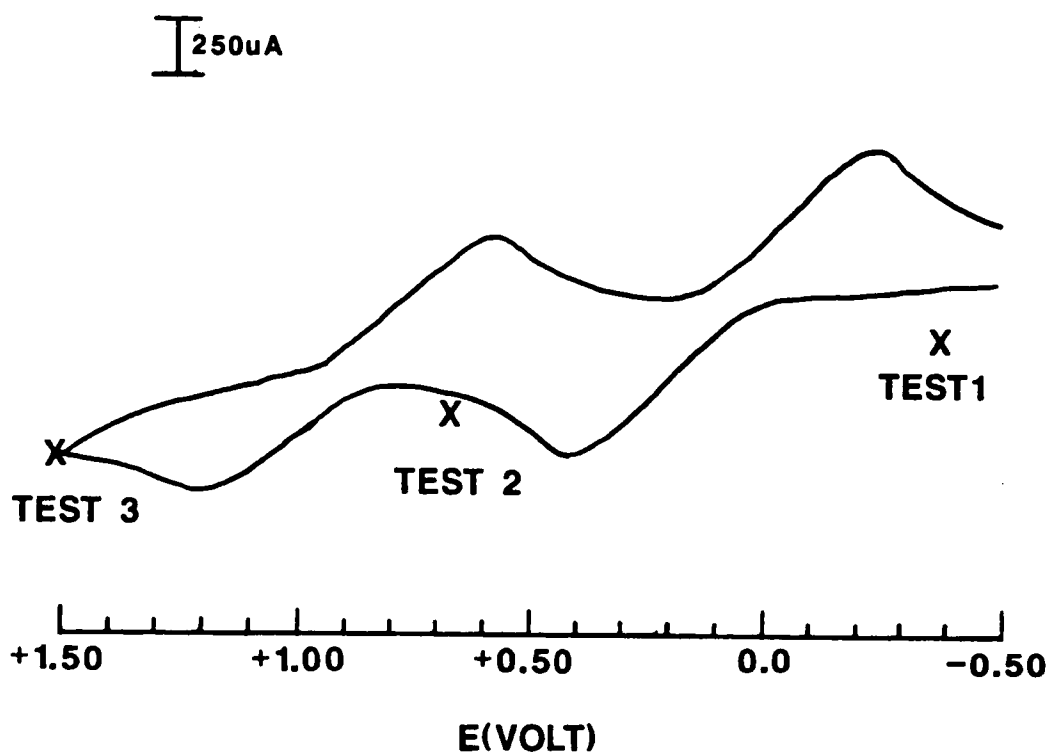


Figure 26. Cyclic voltammogram, obtained in the IR spectro-electrochemical cell, of 10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})]-(\text{PF}_6)$, 25, in $\text{CH}_2\text{Cl}_2/0.1$ M TBAH.

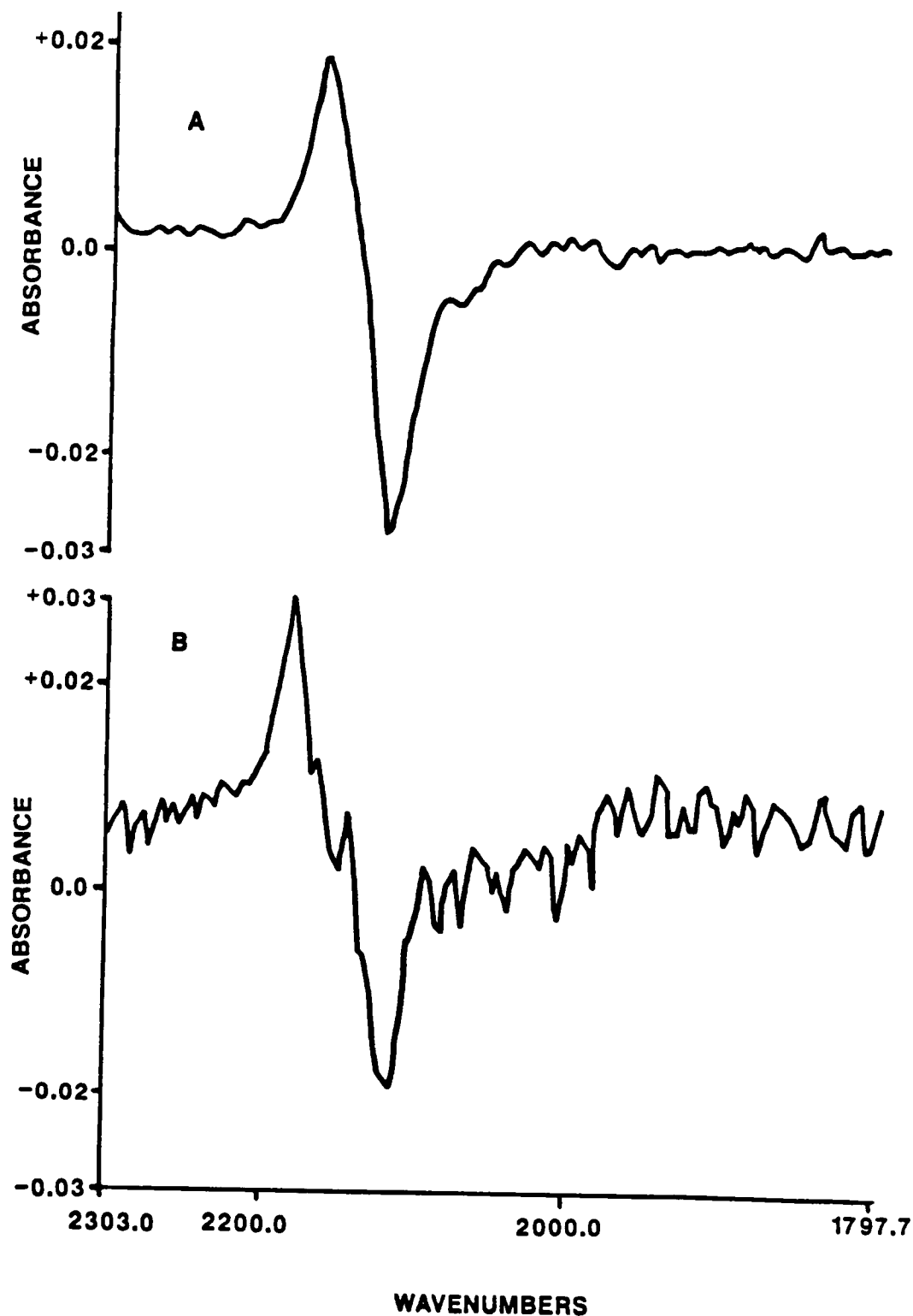


Figure 27. Potential difference IR spectra of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)$, 25, at (a) -0.4 and +0.6 V, and (B) -0.4 and +1.5 V.

Frozen-solution IR spectra of thermochromic and non-thermochromic species were obtained in an attempt to determine if a metal-to-ligand or ligand-to-metal charge transfer occurs. Changes in CN stretching frequencies were observed upon freezing. Room-temperature and frozen-solution IR spectra of the paramagnetic non-thermochromic species, 38, reveal an increase of 5 cm^{-1} from 2176 to 2181 cm^{-1} upon freezing. The frozen and room-temperature solution IR spectra of 29, a diamagnetic species, reveals an increase of 7 cm^{-1} in the CN stretching frequency from 2124 to 2131 cm^{-1} upon freezing. The room-temperature and frozen-solution IR spectra of 25 and 35 were also obtained. Upon freezing a solution of 35, an increase of 8 cm^{-1} occurs in the CN stretch from 2172 to 2180 cm^{-1} . Freezing a solution of 25 results in an increase of 6 cm^{-1} in the CN stretching frequency from 2122 to 2128 cm^{-1} . A room-temperature and frozen-solution IR spectra of 37, another species that displays thermochromism, exhibit an increase of 7 cm^{-1} in the CN band from 2172 to 2179 cm^{-1} upon freezing.

The mixed-valence species, 35, shows a larger increase in the CN stretching frequency than 38, 8 cm^{-1} vs 5 cm^{-1} , upon freezing; whereas the dinuclear Rh(I) parent compounds all show a similar increase in the CN stretching frequency. The frozen solution IR spectrum of 35, however, did not result in the CN frequency increasing to 2189 cm^{-1} , that of the electrochemically generated $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{4MPz})](\text{PF}_6)_3$ species.

If a metal-to-ligand charge transfer is occurring upon freezing, the increased electron density on the pyrazolate ligand

would increase the electron-donating ability of the pyrazolate ion into the rhodium $d \pi$ orbitals. Since the pyrazolate π orbitals and the carbon π^* orbitals of the t -BuNC ligands interact with the same rhodium $d \pi$ orbitals, a delocalization of electron density from the pyrazolate to the isocyanide ligands would occur. A possible consequence of this delocalization is the CN stretching frequency not approaching the stretching frequency observed in the Rh(II) dimer. Although the CN bands increase upon freezing, the increase is small and therefore is not conclusive evidence for a metal-to-ligand charge transfer. Another possible cause of the observed thermochromic effect is a structural rearrangement of the dinuclear species upon freezing.

The room-temperature solution ESR spectrum of 66 reveals an isotropic signal at a g -value of 2.13. The room-temperature ESR spectra of 69 and 70 are anisotropic, with components at g -values of 2.12 and 2.16 for 69, and 2.16 and 2.20 for 70 (Figure 28). The g -values obtained for 66, 69 and 70 suggest that the unpaired electron is essentially metal-based. The frozen solution spectra of 66-70 in a 4:1 CH_2Cl_2 /toluene solution are shown in Figures 29-31. These spectra resemble that of 38 but do not exhibit hyperfine splitting. The frozen-solution spectra of 66-70 are interpreted as those of orthorhombic systems with observable components at g values of 2.175 ± 0.015 , 2.14 ± 0.01 and 2.04 ± 0.02 (Table XIII). These g -values are consistent with a metal-centered unpaired electron. The frozen-solution ESR spectra of 66, 68 and 70 also reveal a signal at $g = 2.0$, which is attributed to an isomer similar to those formed in

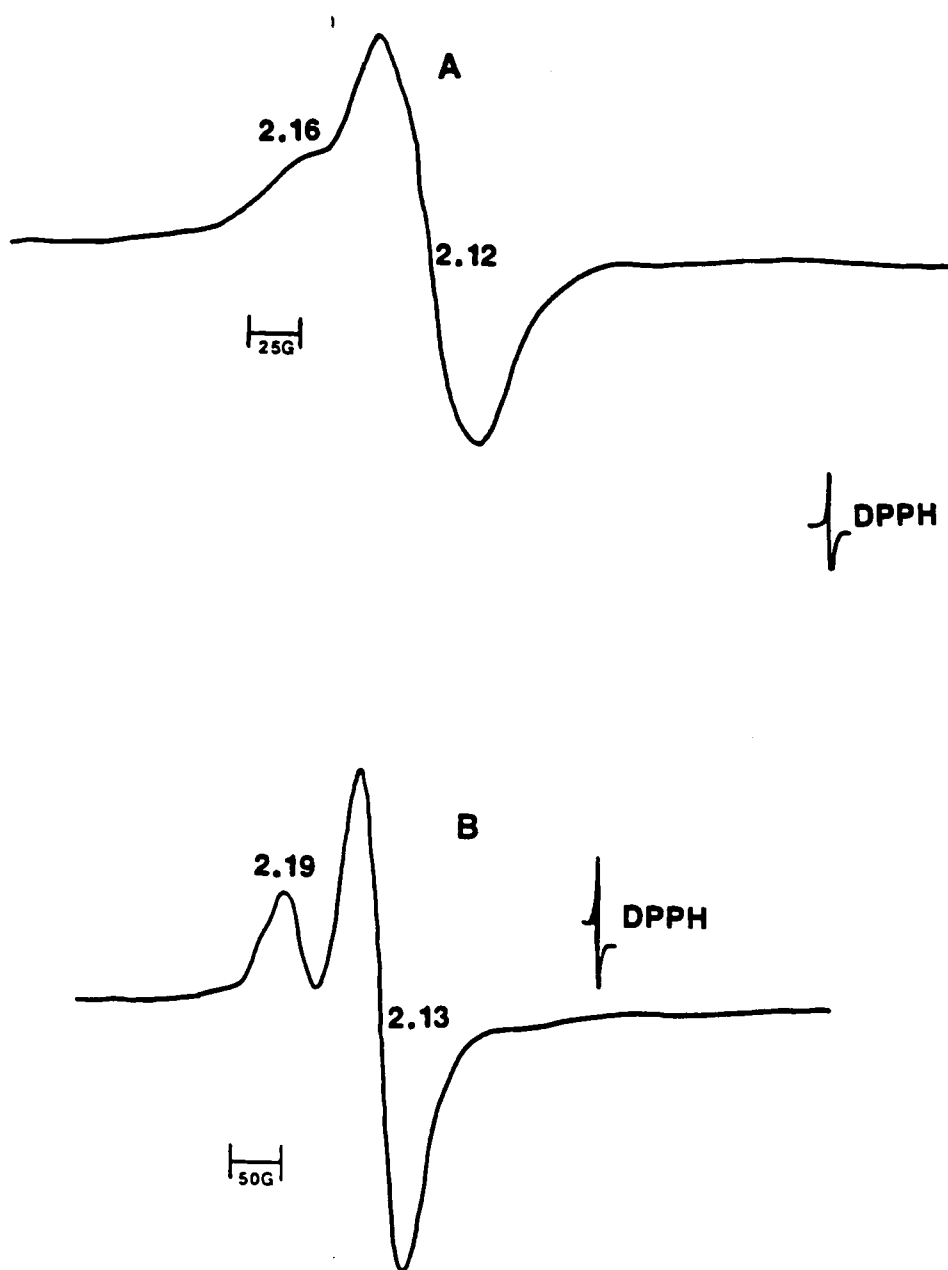


Figure 28. Room-temperature ESR spectra of CH_2Cl_2 solutions of (A) $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4B35MPz})](\text{PF}_6)_2$, 69, and (B) $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-345BPz})](\text{PF}_6)_2$, 70.

TABLE XIII

ESR DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Z})](\text{PF}_6)_2$

Z	<u>Low field</u>	<u>Intermediate field</u>	<u>High field</u>
	g	g	g(A) ^a
Pz, <u>66</u>	2.18 ^b 2.13 ^b		2.02 ^b (1.3 x 10 ⁻³) 2.00 ^b
4MPz, <u>67</u>	2.16 ^c		2.03 ^c
35MPz, <u>68</u>	2.18 ^b 2.15 ^b	2.06 ^b	2.00 ^b
4B35MPz, <u>69</u>	2.16 ^c 2.14 ^c	2.05 ^c 2.07 ^d	 2.01 ^d 1.99 ^d
345BPz, <u>70</u>	2.19 ^c 2.13 ^c		2.02 ^c 2.00 ^c

^a A value given in cm⁻¹

^b 4:1 CH₂Cl₂/toluene solutions at -160 °C

^c 4:1 CH₂Cl₂/toluene solutions at -196 °C

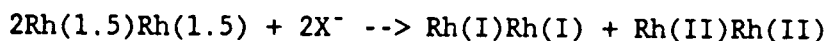
^d 4:1 CH₂Cl₂/ethanol solution at -196 °C

complexes 34-37 upon freezing. The component at a g-value of approximately 2.18 is attributed to interaction along the $\text{Rh}_2\text{N}_2\text{C}_2$ magnetic axis, and the component at 2.14 is attributed to interaction along the Rh_2P_4 magnetic axis. The component at approximately 2.04, attributed to interaction along the Rh-Rh magnetic axis, only shows hyperfine splitting due to coupling to two equivalent rhodium atoms in the frozen-solution ESR spectrum of 66. The ESR spectrum of 66 at -160°C shows a semi-resolved triplet with $A = 1.3 \times 10^{-3} \text{ cm}^{-1}$ for the signal at $g = 2.02$ (Figure 29A).

A thermosolvent effect is observed when the ESR spectrum of 69 is obtained in a 4:1 CH_2Cl_2 /ethanol solution. As stated earlier, the ESR spectrum of 69 in a CH_2Cl_2 /toluene solution exhibits resonances with g values at 2.16, 2.14 and 2.05 (Figure 31A); but in a CH_2Cl_2 /ethanol solution, the spectrum is similar to the ESR spectrum of 34-37 at 77 K. As illustrated in Figure 31B, the ESR spectrum in CH_2Cl_2 /ethanol at 77 K reveals three components with g values of 2.07, 2.01 and 1.99.

E. Electron-Transfer Reactions Involving Some Electrochemically-Generated Species

The chemical reactivity of the mixed-valence species includes disproportionation and electron-transfer reactions. In the presence of coordinating-anionic ligands that can stabilize the dinuclear rhodium(II) framework, the mixed-valence species undergoes an instantaneous disproportionation reaction:



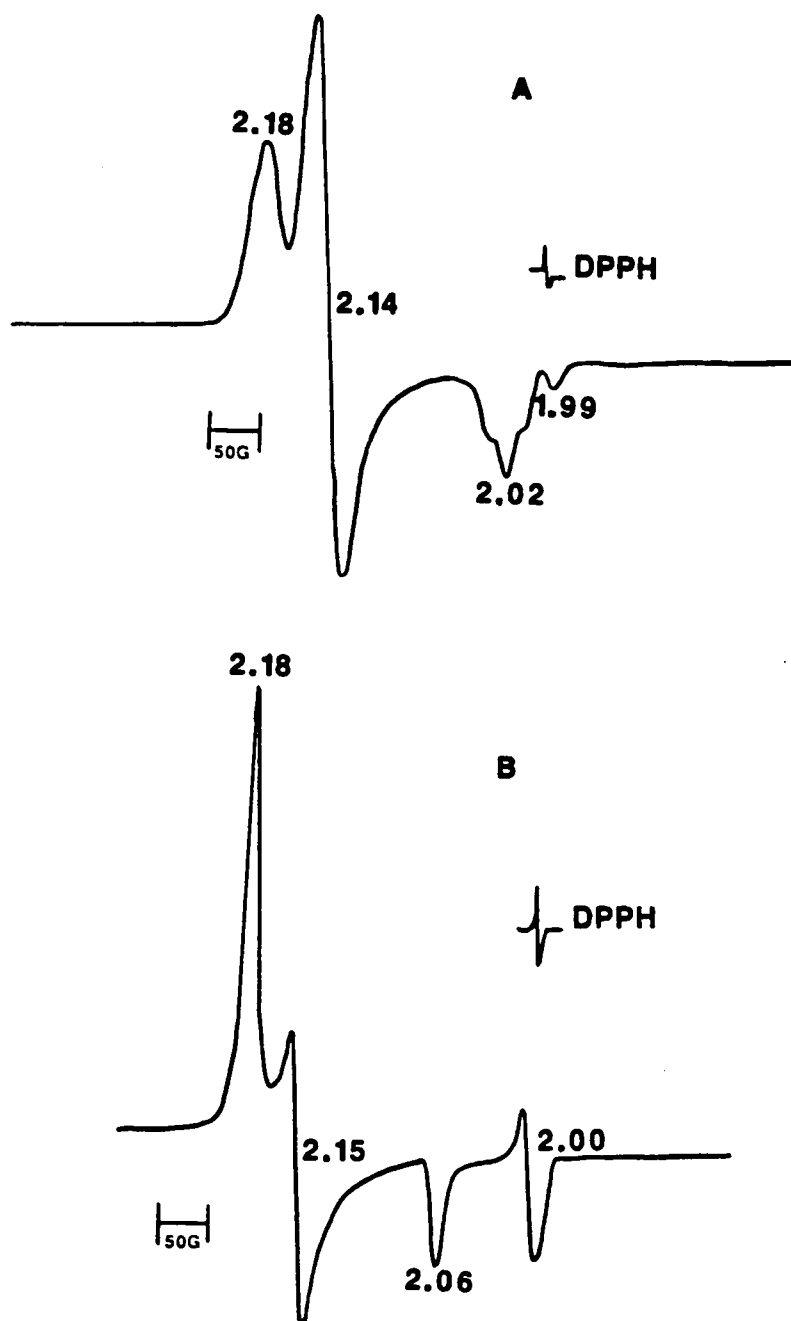


Figure 29. ESR spectra of 4:1 CH_2Cl_2 /toluene solutions at -160°C of (A) $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Pz})](\text{PF}_6)_2$, 66, and (B) $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-35MPz})](\text{PF}_6)_2$, 68.

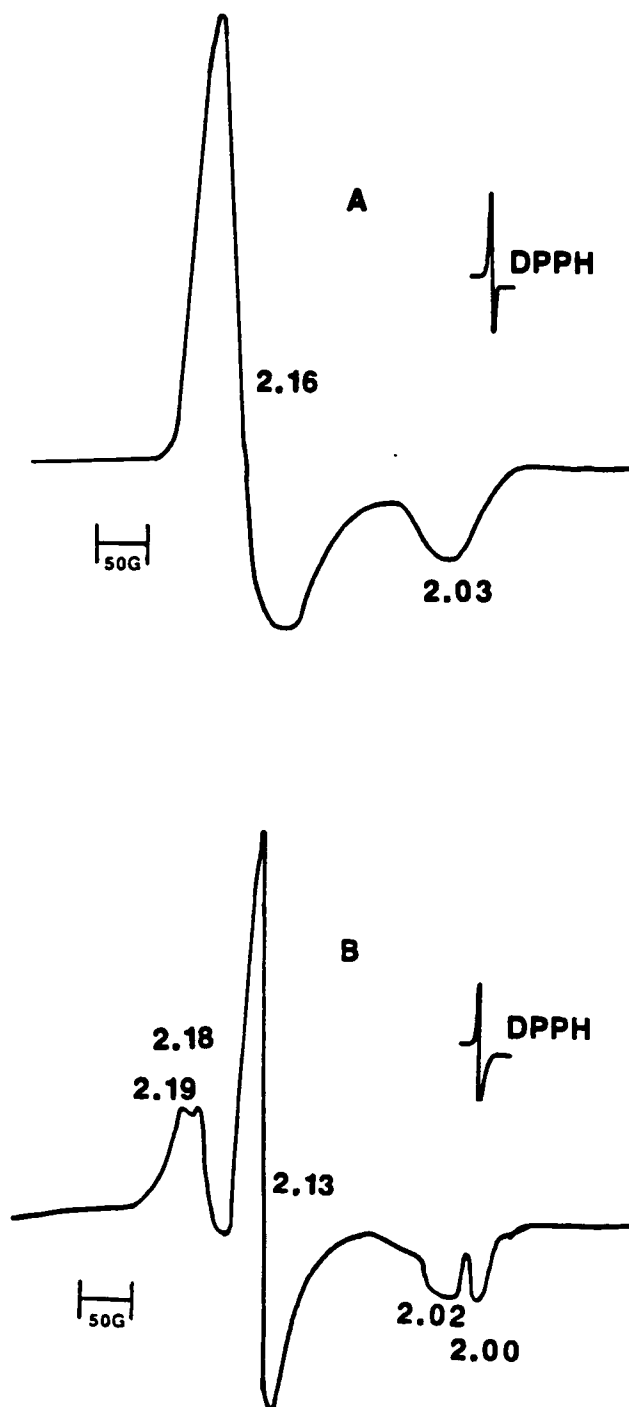


Figure 30. ESR spectra of 4:1 CH_2Cl_2 /toluene solutions at 77 K of (A) $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4MPz})](\text{PF}_6)_2$, 67, and (B) $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-345BPz})](\text{PF}_6)_2$, 70.

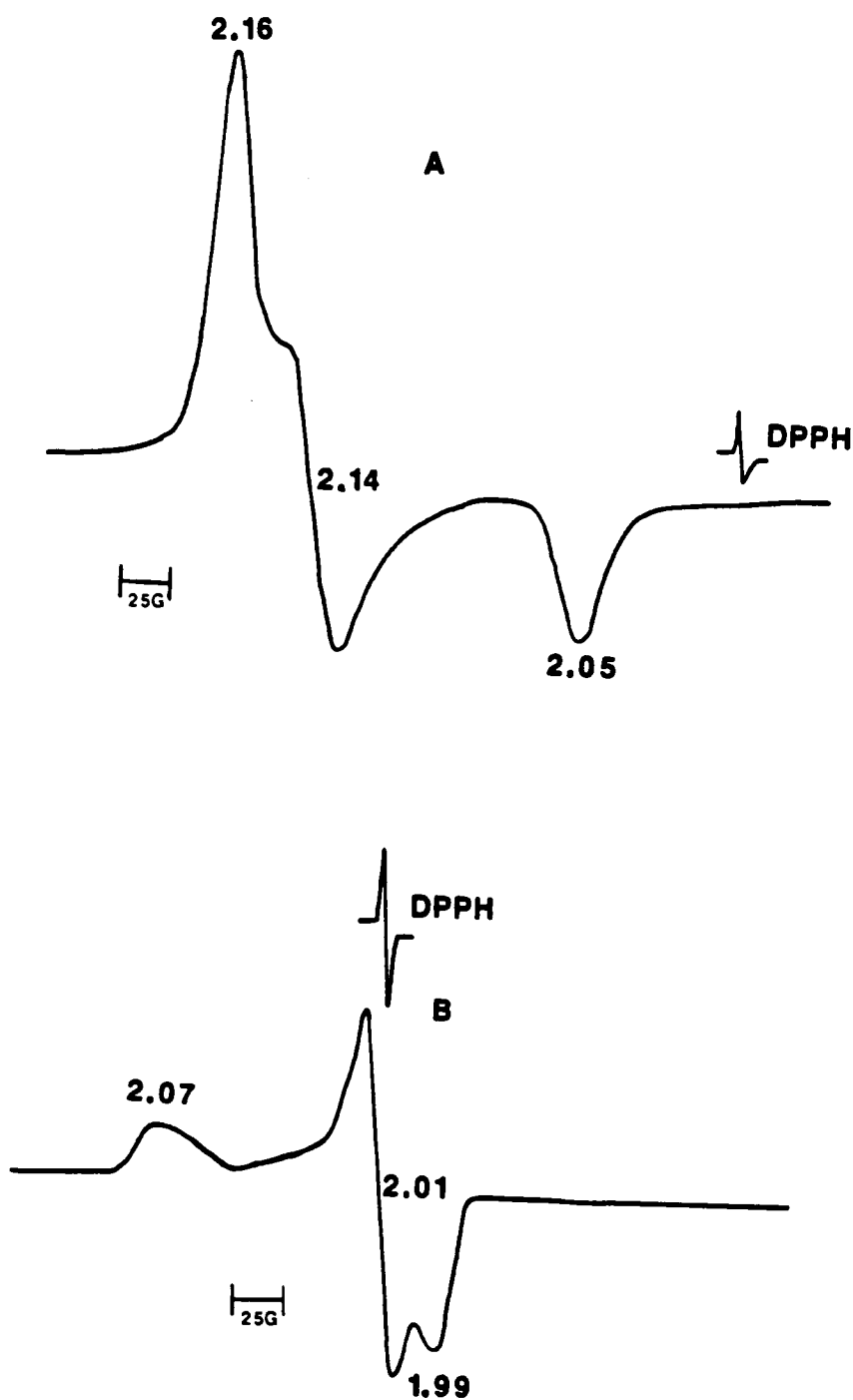


Figure 31. Frozen-solution ESR spectra of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4B35MPz})](\text{PF}_6)_2$, 69, in a 4:1 (A) CH_2Cl_2 /toluene, and (B) CH_2Cl_2 /ethanol solutions at 77 K.

Upon addition of one equivalent of Br^- to 34, the solution changes color instantaneously from green to orange. The $^{31}\text{P}(\text{H})$ NMR spectrum of the orange solution reveals the presence of two species, both exhibiting an $\text{AA}'\text{A}''\text{A}''' \text{XX}'$ spin system. The chemical shift and $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 5.2 ppm and 92.8 Hz are identical to those of 44, while the values of 22.7 ppm and 141.6 Hz of the second species are identical to those of 24. The formation of a Rh(I) and Rh(II) dimer from a dinuclear Rh(1.5) species indicates that a disproportionation reaction was induced by the bromide ion.

Compounds 37, 38 and 39 have all been shown by $^{31}\text{P}(\text{H})$ NMR spectroscopy to disproportionate in the presence of chloride ions. Compound 39 disproportionates to 27 and 43 in the presence of chloride ions; for 37 and 39, the disproportionation reaction yields 28, 29 and presumably $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Z})](\text{PF}_6)$ ($\text{Z}=\text{4B35MPz}, \text{345BPz}$). The chloro complexes containing 4B35MPz and 345BPz both exhibit $\text{AA}'\text{A}''\text{A}''' \text{XX}'$ patterns with chemical shifts of 10.7 and 10.1 ppm, respectively. The $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 92.8 Hz is obtained for both species.

Disproportionation reactions have also been observed for 66 and 69 in the presence of chloride ions. As determined by $^{31}\text{P}(\text{H})$ NMR, both species generate the parent compound and presumably $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{Cl}_2(\mu\text{-Z})](\text{PF}_6)$ ($\text{Z}=\text{Pz}, \text{4B35MPz}$). The $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 83.01 Hz for both dinuclear Rh(II) species is in the range observed for similar halogenated dicarbonyl complexes.⁸¹ The chemical shifts for the chlorinated species generated by the disproportionation reaction of 66 and that by treating 18

with Cl₂ are 11.35 and 10.68 ppm, respectively. The difference results from the four position of the pyrazolate ligand being chlorinated when 18 is treated with Cl₂.

In the presence of Br⁻, 66, 69 and 70 disproportionate to form a dinuclear Rh(I) and Rh(II) species. Since the oxidation wave of bromide ($E^0 = +0.846$)⁹² and the reduction wave of the dinuclear Rh(1.5) complexes occur in the same potential range, the oxidation of Br⁻ to form Br₂ cannot be neglected. Oxidation of bromide by a mixed-valence compound generates the dinuclear Rh(I) complex and Br₂. The Br₂ formed then reacts with the dinuclear Rh(I) complex producing the brominated dinuclear Rh(II) complex. The extent to which this mechanism operates has yet to be determined. For 69 and 70, the disproportionation generates 22 and 23 as the dinuclear Rh(I) species with [Rh₂(μ-dppm)₂(CO)₂Br₂(μ-4B35MPz)](PF₆)⁸¹ and presumably [Rh₂(μ-dppm)₂(CO)₂Br₂(μ-345BPz)](PF₆) as the dinuclear Rh(II) species. However, for 66 the addition of one equivalent of Br⁻ yields 18 and [Rh₂(μ-dppm)₂(CO)₂Br₂(μ-4BPz)](PF₆)⁸¹. The formation of [Rh₂(μ-dppm)₂(CO)₂Br₂(μ-4BPz)](PF₆) demonstrates that Br⁻ is oxidized to Br₂, which then reacts with 18 to form the dinuclear Rh(II) compound. The addition of one equivalent I⁻ to 67 yields 20 and [Rh₂(μ-dppm)₂(CO)₂I₂(μ-4MPz)](PF₆)⁸¹ as determined by ³¹P{H} NMR data. Since the oxidation of I⁻ ($E^0 = 0.29$ V)⁹² occurs at a less-positive potential than the reduction of 67, the mechanism operating in the formation of the dinuclear Rh(I) and Rh(II) species, which includes the oxidation of I⁻ to I₂, is enhanced.

Electron-transfer reactions between two different dirhodium

complexes have been observed by UV-Vis spectroscopy. The addition of a dirhodium(I) to a dirhodium(1.5) compound, in which the dirhodium(I) complex contains an oxidation wave at a less-positive potential than the cathodic wave of the dinuclear Rh(1.5) compound, results in an electron-transfer reaction producing dirhodium(1.5) and dirhodium (I) compounds, respectively.

The UV-Vis spectrum of $[\text{Rh}_2(\mu\text{-dapm})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)_2$ ⁸⁶ reveals an absorption maximum at 434 nm. Upon addition of 24 in increments of 0.25 equivalents, a band at 502 nm due to $[\text{Rh}_2(\mu\text{-dapm})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)$ appears (Figure 32A). The band at 434 nm increases continuously while shifting toward 427 nm, which is attributed to the formation of 34. After the addition of one equivalent of 24, the band at 427 nm exhibits no increase in absorbance or shift in wavelength (Figure 32B). The absorbance at 427 nm does not increase since 34 can no longer be generated due to the consumption of $[\text{Rh}_2(\mu\text{-dapm})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)_2$. Up to the addition of one equivalent, the absorbance in the 430 nm region increases continuously since the extinction coefficient of 34 is 1.4 times that of $[\text{Rh}_2(\mu\text{-dapm})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)_2$, 34,000 vs 24,000. The absorbance at 502 nm increases continuously until one equivalent of 24 has been added. After the addition of one equivalent of 24, the band at 505 nm shifts toward 514 nm and is attributed to excess 24 (Figure 32B). The band increases continuously since the absorbance is due to $[\text{Rh}_2(\mu\text{-dapm})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)$, formed via the electron-transfer reaction and excess 24. The UV-Vis spectra also show a band at approximately 309 nm

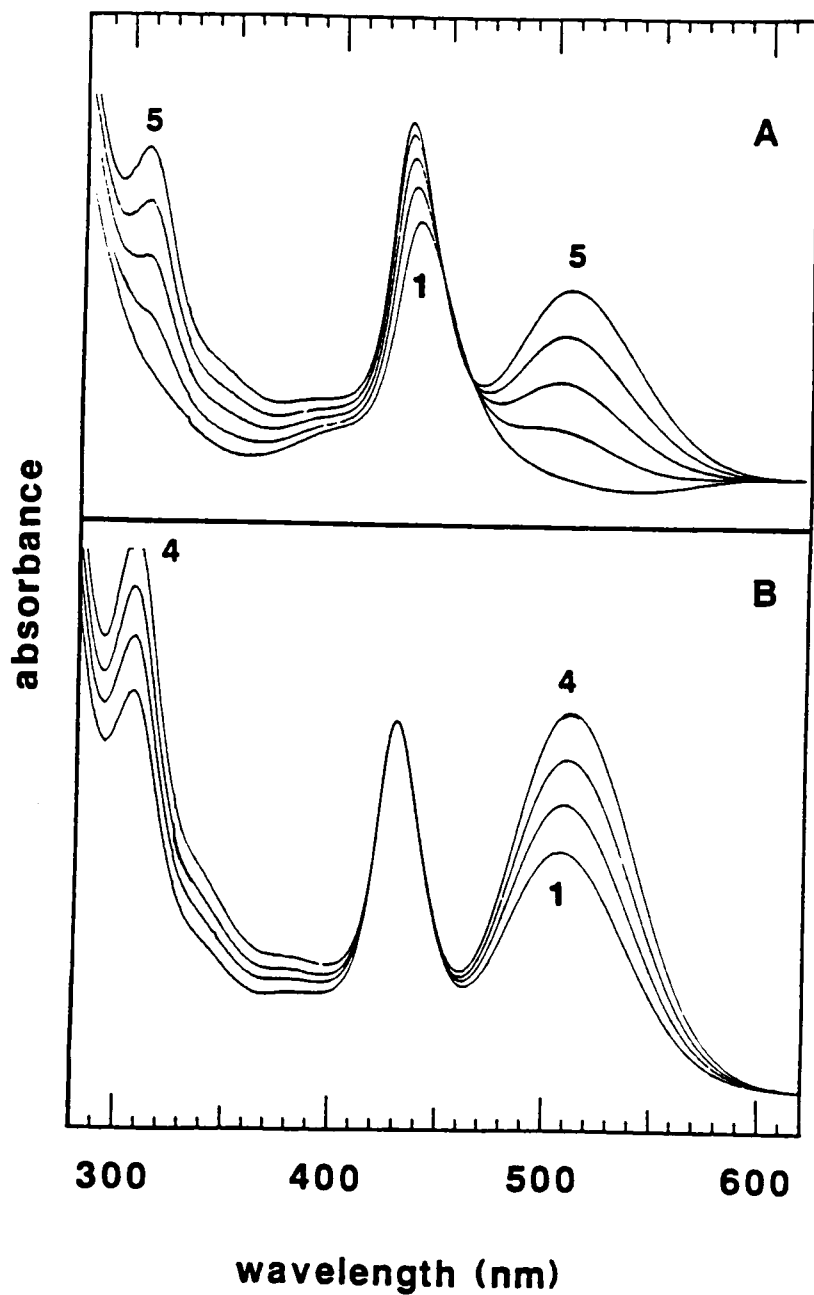
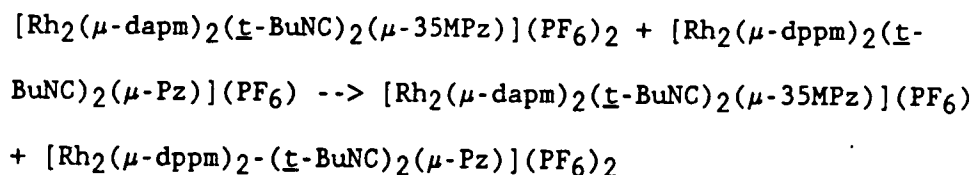


Figure 32. UV-Vis spectral changes accompanying the addition of (A) 0-1 equivalents, and (B) 1-2 equivalents of 24 to a CH_2Cl_2 solution of $[\text{Rh}_2(\mu\text{-dapm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$.

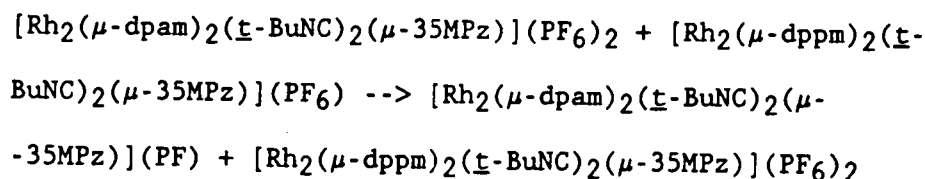
which appears after the addition of the first aliquot of 24. This band is attributed to both Rh(I) dimers. The monitoring of the bands in the region of 430 and 504 nm demonstrates that the following electron-transfer reaction has occurred.



A similar electron-transfer reaction between $[\text{Rh}_2(\mu\text{-dpam})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)_2$ ⁸⁶ and 26 has also been demonstrated by UV-Vis spectroscopy. The UV-Vis spectrum of $[\text{Rh}_2(\mu\text{-dpam})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)_2$ reveals a band at 444 nm. Addition of 0.25 equivalents of 26 results in an increase in absorbance of the band at 444 nm, which simultaneously shifts toward 430 nm. This behavior is attributed to the formation of 36 via electron-transfer reaction. An absorbance at 493 nm appears after the addition of the first aliquot of 26, a result of the formation of $[\text{Rh}_2(\mu\text{-dpam})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)$. The continued increase of the absorbance between 430 and 444 nm is a consequence of the larger extinction coefficient of 36 compared to that of $[\text{Rh}_2(\mu\text{-dpam})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)_2$, 14,000 vs 25,000, respectively.

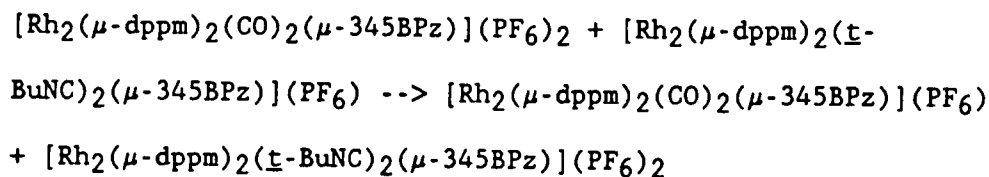
After one equivalent of 26 was added, the absorbance in the 430 nm region does not increase since $[\text{Rh}_2(\mu\text{-dpam})_2(\underline{\text{t-BuNC}})_2(\mu\text{-35MPz})](\text{PF}_6)_2$ has been consumed. The band at 493 nm also shifts toward 505 nm as increasing amounts of excess 26 are added. The

band at 505 nm is attributed to the presence of excess 26. The monitoring of the UV-Vis band in the region attributed to the dinuclear Rh(I) and Rh(1.5) compounds demonstrates that the following electron-transfer reaction has occurred.



Finally, an electron-transfer reaction between a dicarbonyl and a diisocyanide complex was observed by UV-Vis spectroscopy. Addition of 0.3 molar equivalents of 29 to a CH_2Cl_2 solution of 70 results in an electron-transfer reaction. Initially, a band at 426 nm is observed for 70, but shifts toward 422 nm as 29 is added. This shift is attributed to the formation of 38, resulting from the oxidation of 29 by 70. The absorbance in this region increases as 29 is added, up to one equivalent, due to the difference in the extinction coefficient of 15,600 for 70 and 19,600 for 38. As 29 is added to a solution of 70, a band at 482 nm develops as a consequence of the reduction of 70, generating 23. As excess 29 is added, the band at 482 nm shifts toward 494 nm. This shift is attributed to excess 29 which is no longer being oxidized since 70 has been consumed. The absorbance in the 482-494 nm region increases continually as 29 is added, first attributed to 23 and then to excess 29.

The data obtained from the UV-Vis spectra demonstrates that the following electron-transfer reaction has occurred.



All electron-transfer reactions are believed to occur through an outersphere mechanism.

With the use of cyclic voltammetry, a comproportionation reaction is observed when 26 is added to a solution containing $[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_3$. Exhaustive controlled-potential electrolysis of a CH_2Cl_2 solution containing 0.1 M TBAH and 26 at +1.3 V generates $[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_3$. The cyclic voltammogram of the oxidized solution is shown in Figure 33A. Upon addition of 0.25 molar equivalents of 26 to the oxidized solution, an instantaneous color change from red-brown to green occurs signifying the formation of the mixed-valence species, 36.

Figure 33 shows an increase in current for the removal of the second electron as aliquots of 26 are added to $\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_3$. Cyclic voltammetric data reveal the absence of current for the removal of the first electron when the potential is initiated from 0.150 V in the positive direction. When the amount of 26 exceeds one equivalent, the color of the solution approaches a purple-red color, and current for the removal of the first electron is observed. The data obtained from the cyclic

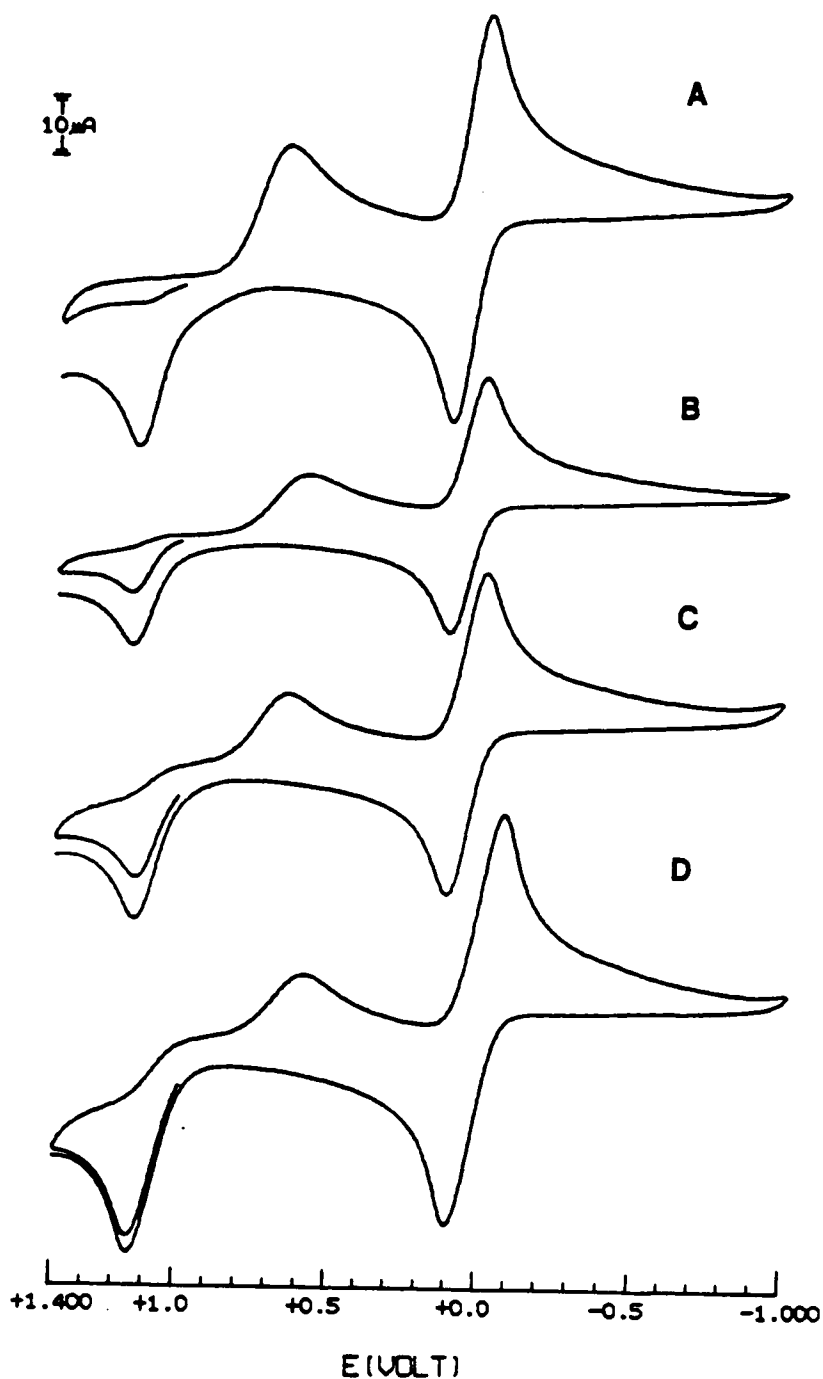
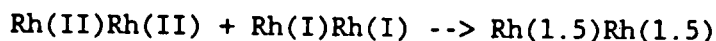


Figure 33. Cyclic voltammograms of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)$, 26, in $\text{CH}_2\text{Cl}_2/0.1$ M TBAH (A) after a two-electron oxidation; followed by the addition of (B) 0.25, (C) 0.50, and (D) 1.00 equivalents of 26.

voltammograms reveals that the following comproportionation reaction has occurred.



F. Electrochemical Behavior of Dirhodium(I) Complexes in the Presence of Coordinating Species

The halide complexes, 40, 42 and 44-52, which were prepared by treating the dinuclear Rh(I) parent compound with the corresponding halogen, can also be prepared electrochemically. The chloride complexes of 26 and 27, which could not be prepared by treating a solution of 26 and 27 with Cl₂, were also electrochemically generated.

Figure 34A shows a cyclic voltammogram of a CH₂Cl₂ solution containing 0.1 M TBAH, 24 and excess TBAI. The cyclic voltammogram reveals an anodic wave at +0.062 V with the corresponding cathodic wave at -0.513 V. Controlled-potential coulometry at +0.10 V indicates that 24 undergoes a two-electron oxidation in the presence of I⁻. The cyclic voltammogram of the oxidized solution reveals a cathodic wave at -0.768 V and the anodic response at +0.003 V (Figure 34B). The IR spectrum of the oxidized product indicates terminal *t*-BuNC ligands with CN stretching frequencies at 2164(s) and 2133(sh) cm⁻¹, and the presence of PF₆⁻ at 839(s) and 557(m) cm⁻¹. The ³¹P(H) NMR spectrum exhibits a symmetrical AA'A''A'''XX' pattern with a [¹J_(Rh-P) + xJ_(Rh-P)] value of 95.2 Hz and a chemical shift of 4.6 ppm. These data are identical to those obtained by

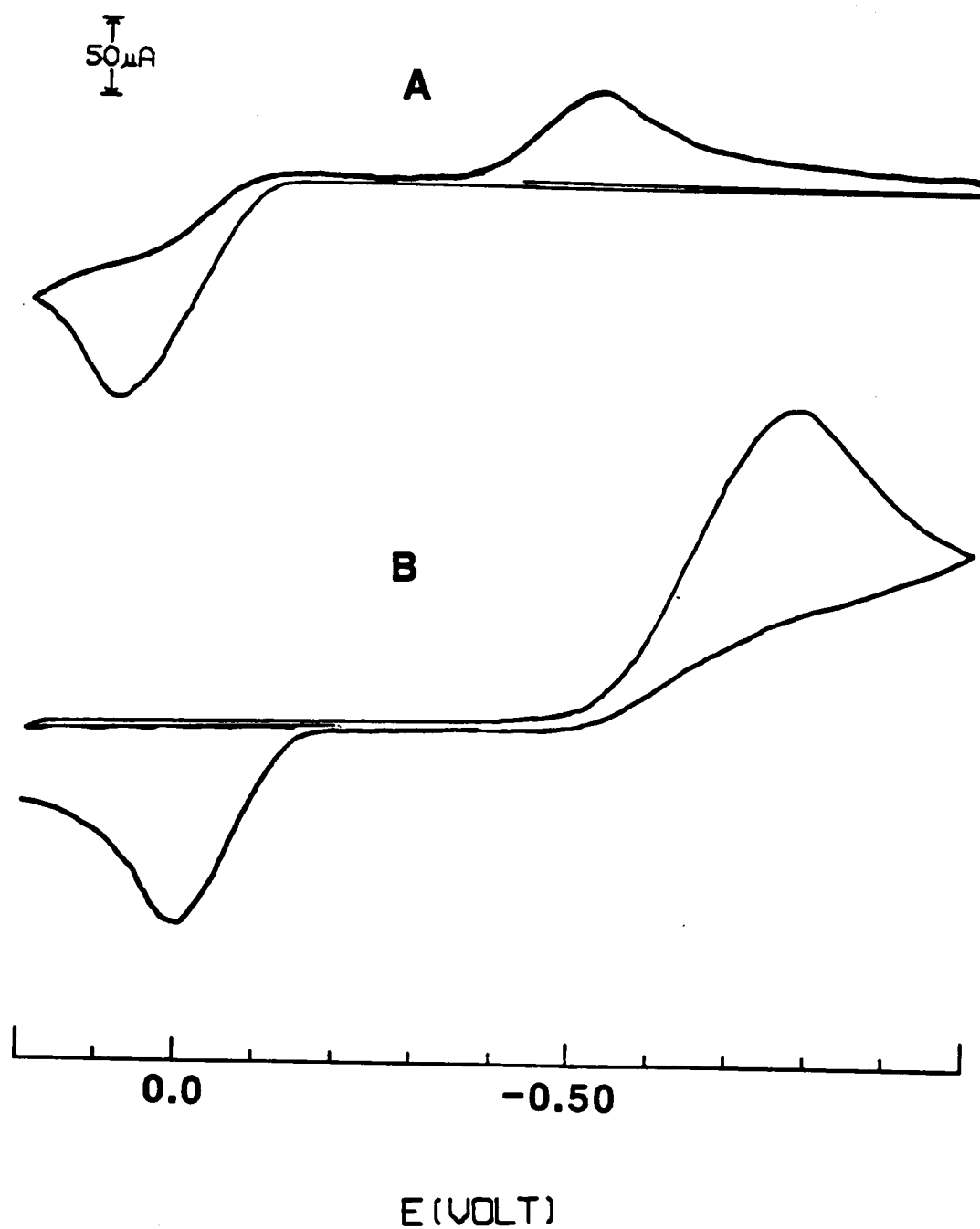


Figure 34. Cyclic voltammograms of 10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Pz})](\text{PF}_6)$, 24, in $\text{CH}_2\text{Cl}_2/\text{TBAH}$ and 5.0×10^{-4} M TBAI, (A) before oxidation, and (B) after oxidation.

treating a CH_2Cl_2 solution of 24 with I_2 , thus the electrochemical oxidation product of 24 in the presence of I^- is formulated as 49.

The cyclic voltammogram shown in Figure 34 is typical of all the dirhodium(I) pyrazolate complexes, 24-27 and 29, investigated in the presence of excess halide ions. The data, given in Table XIV, show the peak potentials for the anodic and cathodic waves before and after bulk oxidation for the electrochemically generated dirhodium(II) complexes containing halide ions. The analytical data obtained for these complexes are identical to those obtained from treating the respective Rh(I) dimer with the appropriate halogen; thus the chemical and electrochemical oxidative addition reactions of 24-27 and 29 generate identical dihalide complexes, 40-52.

The UV-Vis data obtained from 40-52 reveal that the lowest-energy transition is shifted to higher energy as the halide ion is changed from the most polarizable (I^-) to the least polarizable (Cl^-) for a given pyrazolate complex (Table XV). The more polarizable halide ion is a better π -donating ligand, and thus increases the electron density on the rhodium atoms. This increased electron density results in increased Rh-Rh interaction, yielding a lower LUMO and a higher HOMO for the iodo compounds, consistent with the observed trends.

As shown in Table V, page 149, the chemical shifts of the halogenated complexes, 40-52, do not demonstrate any consistent trends. For the pyrazolate and 4-methylpyrazolate complexes, the chemical shifts increase in the order $\text{Cl}^- < \text{I}^- < \text{Br}^-$. For 3,5-dimethylpyrazolate, the order is $\text{I}^- < \text{Br}^- < \text{Cl}^-$ and for triazolate,

TABLE XIV

ANODIC AND CATHODIC PEAK POTENTIALS FOR
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Z})](\text{PF}_6)$ COMPLEXES IN THE
 PRESENCE OF EXCESS X^-

Z	X-	<u>Before Oxidation</u>	<u>After Oxidation</u>
		anodic/cathodic, V	cathodic/anodic, V
Pz, <u>24</u>	Cl	0.070/-0.779	-0.814/-0.002
	Br	0.023/-0.676	-0.740/-0.027
	I	0.062/-0.513	-0.768/ 0.003
4MPz, <u>25</u>	Cl	0.017/-0.775	-0.935/-0.034
	Br	0.015/-0.685	-0.796/-0.019
	I	0.028/-0.607	-0.745/-0.031
35MPz, <u>26</u>	Cl	0.003/-0.993	-1.079/-0.052
	Br	0.015/-0.770	-0.840/-0.015
	I	-0.007/-0.683	-0.780/-0.025
Tz, <u>27</u>	Cl	0.123/-0.662	-0.712/ 0.072
	Br	0.180/-0.561	-0.727/ 0.127
	I	0.118/-0.486	-0.538/ 0.041
345BPz, <u>29</u>	Br	0.020/-0.804	-0.721/-0.038

TABLE XV

LOWEST ENERGY UV-VIS TRANSITION FOR
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{X}_2(\mu\text{-Z})](\text{PF}_6)$ COMPLEXES

Z	X	λ_{max} , nm	Z	X	λ_{max} , nm
Pz	Cl	464	35MPz	Cl	464
	Br	473		Br	483
	I	507		I	521
4MPz	Cl	451	Tz	Cl	457
	Br	478		Br	472
	I	512		I	511

the order is $\text{Cl}^- < \text{Br}^- < \text{I}^-$. The 3,5-dimethylpyrazolate complexes follow the same pattern as those of the dicarbonyl complexes, thus revealing that Cl^- is deshielding the phosphorus atoms of the dppm ligand resulting in a downfield chemical shift. For the triazolate complexes, the opposite trend is observed, which follows the same pattern observed for mononuclear complexes.⁹³ The bromide ligand appears to deshield the phosphorus atoms in the 4-methylpyrazolate and pyrazolate complexes, resulting in the downfield chemical shift. The lack of any systematic trends demonstrates that steric, as well as electronic factors, play a role in determining the electron environment around the phosphorus atoms in the dppm ligands. It has been noted⁹⁴ that chemical shift relationships do not reflect phosphorus electron density changes in a simple manner, and over a large range of compounds, empirical correlation of such shifts breaks down.

The reduced $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$ values for complexes 40-52, compared to their parent compound, signify the formation of a Rh-Rh bond. As stated in Chapter III, the general trend for the values of the coupling constant in dppm dirhodium complexes is: (1) for complexes with a Rh-Rh bond, the values are in the range of 90-115 Hz, and (2) for those complexes with no Rh-Rh bond, the values are in the range of 125-140 Hz.^{10,13-15}

Electrochemical oxidative-addition reactions were extended to include a pseudohalogen, thiocyanate, as the coordinating ligand. Thiocyanate (SCN^-), an ambidentate ligand, can coordinate to a metal

center through the nitrogen, sulfur or both when it bridges two metal centers.

M-SCN-M

Generally, nitrogen coordination occurs with class A metals (Cr, Mn, Fe, Co, Ni, Cu, Zn), and sulfur coordination with class B metals (Rh, Pd, Ag, Cd, Ir, Pt, Au, Hg).^{95,96} However, other factors such as steric consideration, the oxidation state of the metal, and the nature of other ligands present in the complex influence whether coordination occurs through the nitrogen or sulfur. Sulfur coordination results in a non-linear M-SCN moiety whereas nitrogen coordination results in a linear moiety.



Consequently, sulfur coordination requires a more open coordination site than nitrogen-bound thiocyanate.

The more electronegative nitrogen atom results in the Π - bonding molecular orbitals polarized toward the nitrogen atom, and the Π^* molecular orbitals polarized toward the sulfur atom. The increase in the Π electron density on the nitrogen atom results in nitrogen functioning as a strong σ and Π donor, and a preference for nitrogen coordination to a metal in a high oxidation state.

Polarization of the empty π^* molecular orbitals toward sulfur affords a strong π -acceptor sulfur atom, and a preference for sulfur coordination when a metal atom is in a low oxidation state or when an electron donor ligand is trans to thiocyanate.⁹⁵

The CN stretching frequency in the IR spectrum has been a diagnostic tool in the assignment of the mode of coordination in thiocyanate. In situations where all electronic and steric factors are constant, the CN stretching frequency occurs at higher wave numbers in the order $-\text{NCS} < -\text{SCN} < -\text{SCN}-$.⁹⁷⁻⁹⁹

The cyclic voltammogram of 24 in a CH_2Cl_2 solution containing 0.1 M TBAH and excess TBASCN reveals an irreversible anodic wave at +0.044 V, and the corresponding cathodic wave at -0.663 V.

Controlled-potential coulometry at +0.10 V indicates that 24 undergoes a two-electron transfer in the presence of SCN^- . The resulting oxidized solution yields a cathodic wave at -0.80 V and an anodic wave at -0.007 V. The IR spectrum of the isolated product reveals three CN bands at 2176, 2091 and 2045 cm^{-1} , and PF_6^- bands at 839 and 557 cm^{-1} . The band at 2176 cm^{-1} is assigned to the CN stretch in t-BuNC, which is in the vicinity of similar dirhodium(II) complexes studied. The bands at 2091 and 2045 cm^{-1} are assigned to sulfur-bound and nitrogen-bound terminal thiocyanate ligands, respectively. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum, shown in Figure 35, reveals a complex pattern centered at approximately 12 ppm. Variable-temperature $^{31}\text{P}\{\text{H}\}$ NMR in the range of +25 - -70 °C in CH_2Cl_2 indicates the occurrence of an exchange process with a coalescence of the phosphorus resonance at -70 °C. The data obtained from the IR

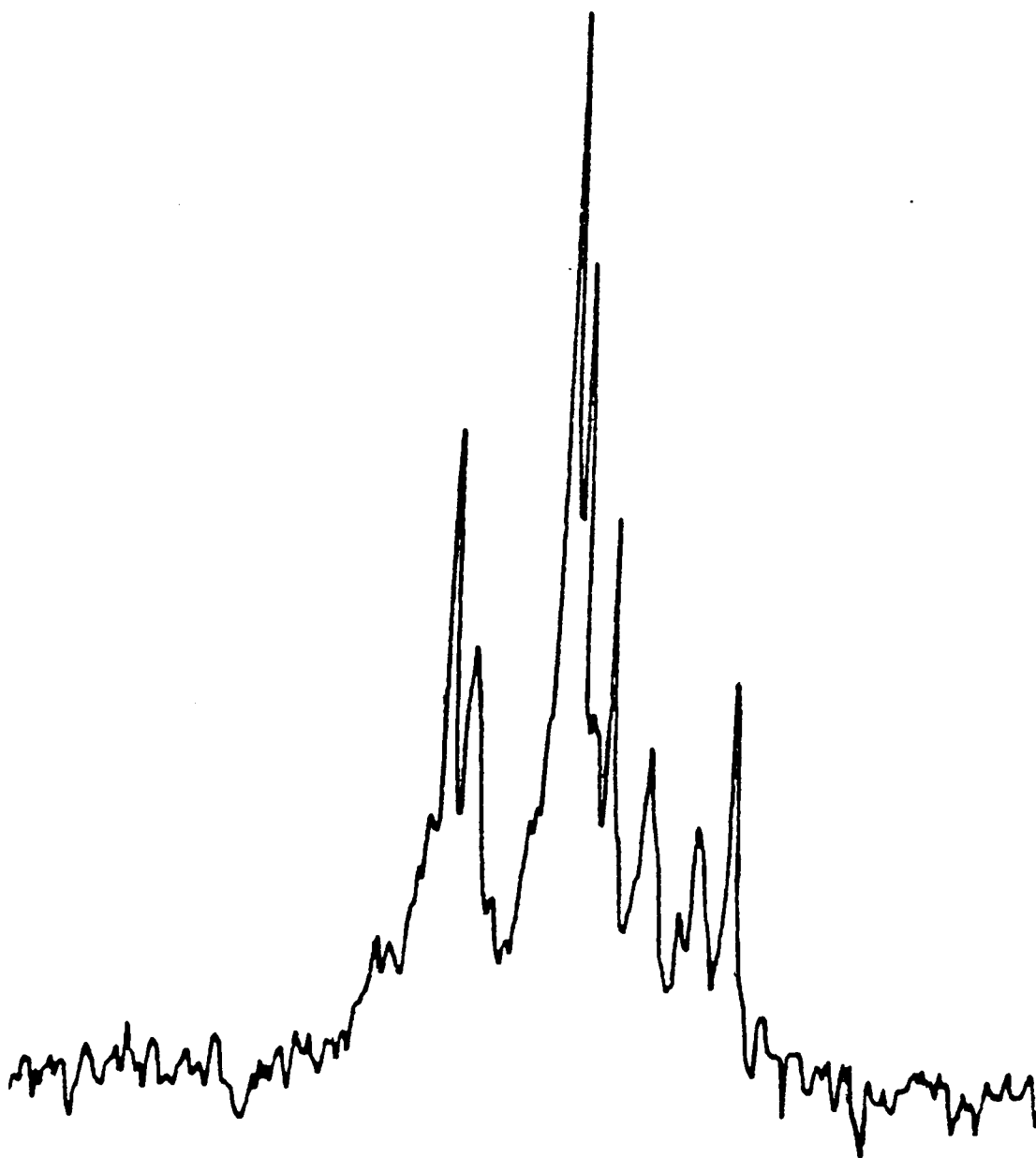
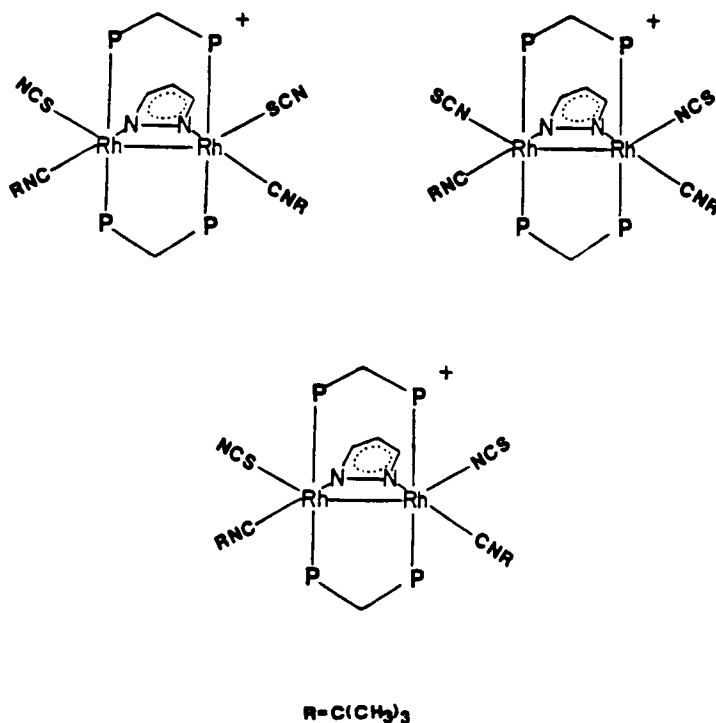


Figure 35. $^{31}\text{P}(\text{H})$ NMR spectrum of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{SCN})_2(\mu\text{-Pz})](\text{PF}_6)$, 53.

and $^{31}\text{P(H)}$ NMR spectra indicate that the product generated from the electrolysis in the presence of SCN^- is formulated as 53, and contains three possible isomers shown below: (a) both thiocyanate ligands coordinating through the sulfur atom, (b) both thiocyanate ligands nitrogen-bound, and (c) one nitrogen-bound and one sulfur-bound thiocyanate ligand.



The anodic and cathodic peak potentials obtained from the cyclic voltammograms of 24-27, in a CH_2Cl_2 solution containing 0.1 M TBAH and excess TBASCN before and after bulk oxidation, are given in Table XVI. The cyclic voltammograms of 24-27 under these conditions

TABLE XVI

ANODIC AND CATHODIC PEAK POTENTIALS FOR
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Z})](\text{PF}_6)$ COMPLEXES
 IN THE PRESENCE OF SCN^-

Z	<u>Before oxidation</u>	<u>After oxidation</u>
	anodic/cathodic, V	cathodic/anodic, V
Pz, <u>24</u>	0.044/-0.663	-0.800/-0.007
4MPz, <u>25</u>	0.022/-0.744	-0.825/-0.021
35MPz, <u>26</u>	-0.008/-0.930	-0.990/-0.016
Tz, <u>27</u>	0.117/-0.580	-0.790/ 0.161

are similar to 24 in the presence of TBAI shown in Figure 34, page 199. The IR data of the isolated products 53-56 are given in Table XVII. The IR spectrum of 56 is the only one which exhibits a weak band attributed to sulfur-bound thiocyanate. The $^{31}\text{P(H)}$ NMR spectra of 53-56 also show complex patterns ascribed to the different isomers present in each product.

Variable-temperature $^{31}\text{P(H)}$ NMR spectra of 54 from +75 to -90 °C was also obtained, and demonstrate a fluxional process (Figure 36). At room-temperature, the lifetime of each isomer is long enough or the exchange process between sulfur and nitrogen bound thiocyanate is slow enough that a phosphorus resonance occurs for all isomers present. At 75 °C, the phosphorus resonance appears as a broad doublet centered at 13.2, and a $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of approximately 85.4 Hz (Figure 36A). The broad doublet indicates a time-average equivalence of the four phosphorus atoms of the dppm ligand. As the temperature is decreased from +25 °C, the $^{31}\text{P(H)}$ NMR spectrum starts to appear as a symmetrical pattern typical of the AA'A''A'''XX' spin system. At -25 °C, the species giving rise to the symmetrical pattern has a chemical shift of 14.3 ppm, and a $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 90.3 Hz (Figure 36B). At -75 °C, a coalescence of the phosphorus resonance into a single broad peak occurs (Figure 36C). Decreasing the temperature from -25 °C, the appearance of a broad resonance could arise from the transformation of the species present at -25 °C into another isomer such that the lifetime of each isomer is reduced, and a broad resonance occurs. This is based on the Heisenberg uncertainty principle, $\Delta E \cdot \Delta t = h$

TABLE XVII

IR DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{SCN})_2(\mu\text{-Z})](\text{PF}_6)$

Z	<u>t-BuNC</u>	<u>-SCN</u>	<u>-NCS</u>
	$\nu\text{CN, cm}^{-1}$	$\nu\text{CN, cm}^{-1}$	$\nu\text{CN, cm}^{-1}$
Pz, <u>53</u>	2176(s)	2091(m)	2045(m)
4MPz, <u>54</u>	2176(s)	2091(m)	2056(m)
35MPz, <u>55</u>	2176(m)	2091(m)	2060(s)
Tz, <u>56</u>	2187(s)	2097(wsh)	2044(s) 2046(sh)

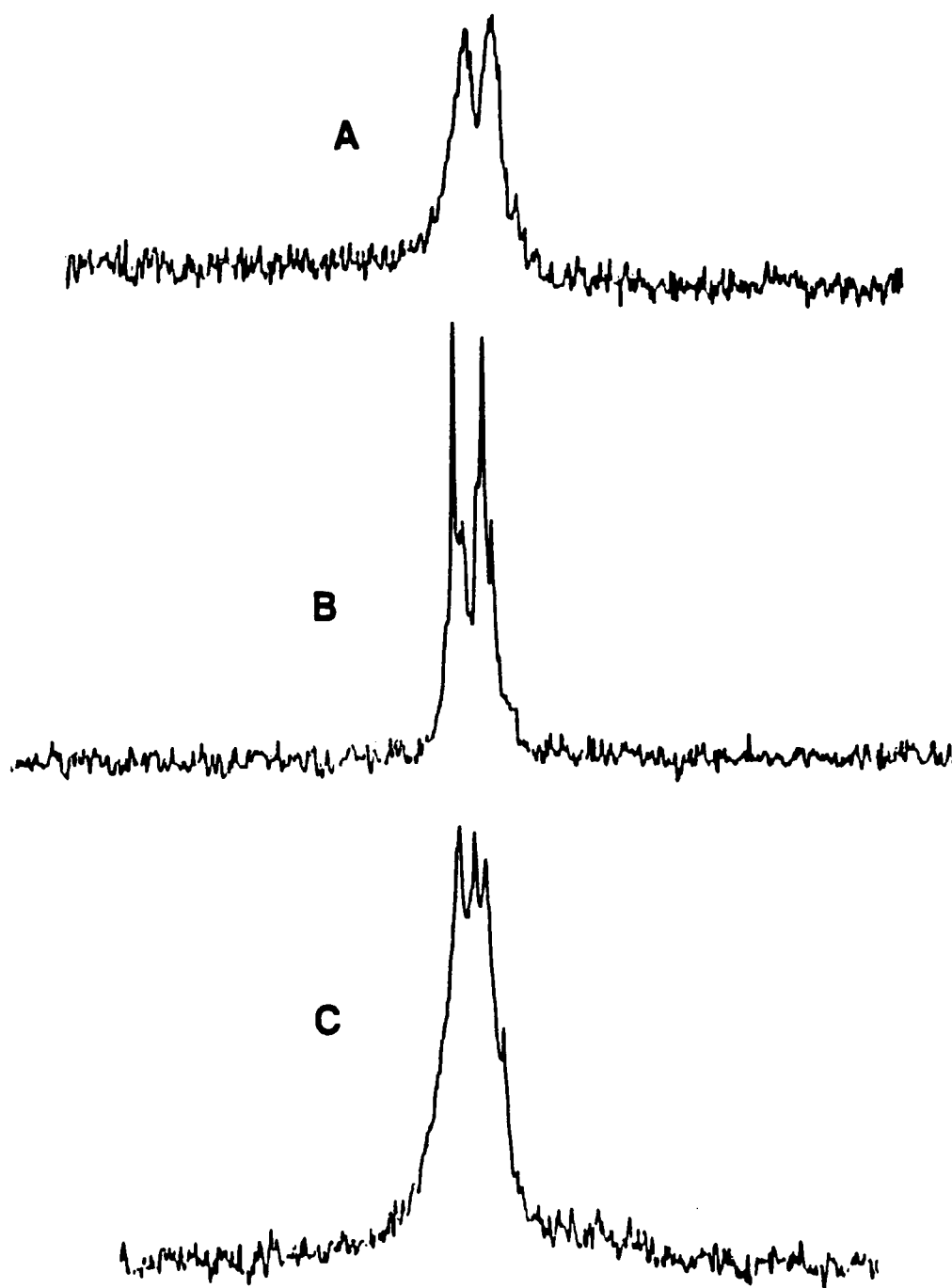


Figure 36. Variable-temperature NMR of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{SCN})_2(\mu\text{-4MPz})](\text{PF}_6)$, 54, at (A) +75 °C, (B) -25 °C, and (C) -75 °C.

where ΔE is the uncertainty in energy corresponding to an uncertainty in Δt . In this case, Δt corresponds approximately to the lifetime (t) of each isomer such that the uncertainty in energy is reflected in an increased line width ($\nu_{1/2}$). As a result, as the lifetime of each state decreases, broadening of the resonance lines occurs.

Compound 53 can also be generated from a disproportionation reaction. Addition of one equivalent of SCN^- to 34 yields 53 and 24 as determined by the $^{31}\text{P}(\text{H})$ NMR spectrum. A disproportionation reaction is also observed when one equivalent of SCN^- is added to a CH_2Cl_2 solution containing 69. The disproportionation reaction generates 22, and presumably $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\text{SCN})_2(\mu\text{-4B35MPz})](\text{PF}_6)$ as determined by the $^{31}\text{P}(\text{H})$ NMR spectrum. The NMR spectrum of the Rh(II) dimer reveals a complex pattern, similar to those obtained for 53-56, indicative of sulfur and nitrogen-bound thiocyanate ligands.

It has been demonstrated that dinuclear Rh(I) complexes can undergo electrochemical oxidative-addition reactions with halides and a pseudohalide to produce dirhodium(II) complexes. The electrochemical behavior of some dirhodium complexes was then extended to include media containing acetate, nitrate and perchlorate ions. These anions have several possible modes of coordination: (a) monodentate, which can coordinate as a bridging or terminal ligand, and (b) bidentate, which can either bridge or chelate the metal atoms.^{97,100,101} All modes of coordination of these anions occur through the oxygen atom.

The cyclic voltammogram of 24 in a CH_2Cl_2 solution containing 0.1 M TBAH and excess TBAAc exhibits an anodic wave at +0.018 V, and a cathodic wave at -1.08 V. Controlled-potential coulometry at +0.150 V indicates that 24 undergoes a two-electron oxidation in the presence of acetate. The cyclic voltammogram of the oxidized solution reveals a cathodic wave at -1.18 V with the anodic response at -0.033 V. The $^{31}\text{P}(\text{H})$ NMR spectrum of the isolated product exhibits an AA'A''A'''XX' pattern with a chemical shift and $[^1J_{(\text{Rh}-\text{P})} + ^xJ_{(\text{Rh}-\text{P})}]$ value of 3.91 ppm and 92.8 Hz, respectively. The IR spectrum indicates the presence of terminal isocyanide ligands with CN stretching frequencies of 2182(s) and 2171(sh) cm^{-1} , and PF_6^- counter-ion bands at 839(s) and 557(m) cm^{-1} . The identity of the product was determined by single crystal structural analysis. Suitable crystals were grown by slow diffusion of ether/hexanes into a CH_2Cl_2 solution containing the oxidized product. Structural analysis of the crystals confirmed the product as $[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t-BuNC}})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)$, 40. Given in Appendix A are: (1) Experimental details, (2) Intensity measurements, (3) Structure solutions and refinement, (4) Positional parameters and their estimated standard deviations, (5) Bond distances, and (6) Bond angles. Anisotropic thermal parameters and calculated and observed structural factors are available.¹⁰²

The crystal structure of 40 consists of a cationic binuclear rhodium(II) complex and a hexafluorophosphate anion in a 1:1 ratio. An ORTEP plot of the dinuclear species with atomic numbering is shown in Figure 37. Complex 40 consists of two Rh(II) d^7 metal

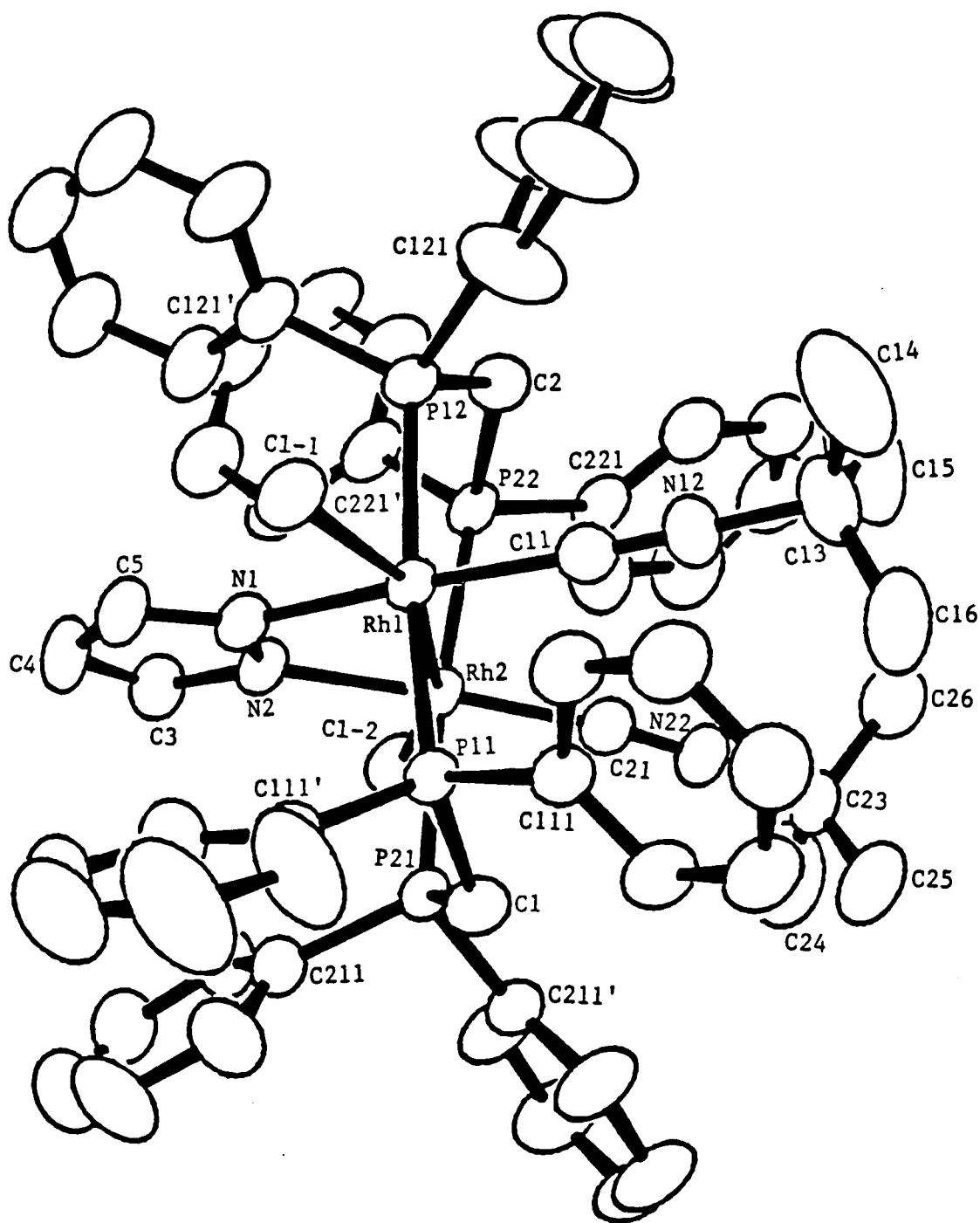


Figure 37. ORTEP plot of $[\text{Rh}_2(\mu\text{-dppm})_2(\pm\text{-BuNC})_2\text{Cl}_2(\mu\text{-Pz})]-(\text{PF}_6)_4$, 40. The hydrogen atoms have been omitted for clarity, and the carbon atoms in the phenyl rings are numbered sequentially around the ring.

centers held together by two trans-bridging dppm ligands, a bridging pyrazolate ligand and a metal-metal bond. Each rhodium atom is located in the center of a distorted octahedron. The octahedral geometry is composed of two trans-phosphorus atoms from the dppm ligands, a nitrogen atom from the pyrazolate ligand, a carbon atom from the isocyanide ligand, chlorine, and the other rhodium atom. The largest distortion from the octahedral geometry arises from the positions of the two chloride ligands. Chlorine atoms 1 and 2 are tilted back, toward the pyrazolate ligand, from the Rh-Rh vector by 23 and 18.5°, respectively. The position of the chloride ligands is probably a result of the bulky t-butyl group on the isocyanide ligand which forces the chloride ligands toward the pyrazolate ligand. In comparison to $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{I}_2(\mu\text{-35MPz})](\text{ClO}_4)$,³¹ the Rh-Rh-C (CO, t-BuNC) angles of 91.8 and 101° for the dicarbonyl species and 40, respectively, are mainly an effect of the terminal CO and t-BuNC ligands. The larger angle observed for 40 results from the t-butyl groups requiring more open coordination sites than the carbonyl ligands. For the dicarbonyl compound, the iodine atoms are tilted toward the pyrazolate ligand from the Rh-Rh vector by only 5.4°, which is a much smaller value than that observed for the chlorine atoms in 40.

The difference in the degree of back-bonding of CO and t-BuNC is observed in the Rh-C (CO, t-BuNC) bond distances of 1.80 and 1.936 Å, respectively. The shorter Rh-C (CO) bond distance demonstrates the stronger back-bonding ability of CO vs t-BuNC. This effect also results in the observed differences in the N-N bond

length in the pyrazolate moiety of 1.35 Å (40) and 1.41 Å (dicarbonyl complex). As shown earlier by the MO description, the pyrazolate π orbitals and the CO or *t*-BuNC π^* orbitals interact with the same rhodium d π orbitals. Therefore, the increased π -acidity of the carbonyl ligands decreases the π -electron density on the pyrazolate moiety. This reduced π -electron density decreases the bond order of the N-N linkage, and a longer bond distance results for the dicarbonyl compound.

A significant structural feature observed for 40, which is not observed in similar trans-dppm dinuclear rhodium complexes, is the folding of the methylene groups of the dppm ligand over the open site opposite the bridgehead position. The pyrazolate ligand and the methylene groups are on opposite sides of the least-square plane composed of the four phosphorus and two rhodium atoms. The effects on the phenyl rings on the same dppm ligand, resulting from the folding of the methylene groups on the opposite side of the pyrazolate ligand are: (1) the phenyl rings on the side of the pyrazolate ligand are forced closer together, (2) the phenyl rings on the side of the isocyanide ligands are forced apart, and (3) the phenyl rings are not parallel (Figure 37). The folding of the methylene groups over the open site opposite the bridgehead position could arise from steric as well as packing factors.

The Rh-Rh separation of 2.768 Å is typical for single metal-metal bond distances for binuclear rhodium A-frames. The larger Rh-Rh separation observed for 40 vs a value of 2.725 Å for $[\text{Rh}_2(\mu\text{-dppm}_2)(\text{CO})_2\text{I}_2(\mu\text{-35MPz})](\text{ClO}_4)^{31}$ presumably arises from the halide

ligands. Chlorine, which is more electronegative and less polarizable than iodine, reduces the electron density between the rhodium atoms. This results in a decrease in the orbital interaction between the two rhodium atoms and a hence larger Rh-Rh separation.

Another notable feature observed in the crystal structure of 40 is revealed in the Rh-P bond lengths. The two phosphorus atoms bound to Rh 1 have bond lengths similar to a Rh(I) dimer, 19 (2.34 Å), and the two phosphorus atoms bound to Rh 2 are similar to a Rh(II) dimer, $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{I}_2(\mu\text{-35MPz})]^+$ (2.388 Å).³¹

All other bond lengths and angles are within expected values for similar rhodium complexes.

In order to determine the source of the chloride ions, the electrolysis was performed with acetone as the solvent. However, a product could not be isolated from an Acetone/TBAH/TBAAc/24 oxidized solution. The supporting electrolyte was then changed to TBAB so a ³¹P(H) NMR spectrum could be obtained on the oxidized solution. The NMR spectrum of the oxidized acetone solution exhibits a symmetrical pattern with a chemical shift and $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 18.4 ppm and 95.2 Hz, respectively. The different NMR data obtained for the oxidized products in CH₂Cl₂ and acetone indicate that the product obtained from the oxidized acetone solution does not contain chloride ligands, and that CH₂Cl₂ is the source of chloride in the CH₂Cl₂ solution. Other data that substantiate this are obtained from disproportionation reactions of 34 with acetate. When the disproportionation reaction is executed in CH₂Cl₂, 24 and 40 are

generated. In acetone, the disproportionation reaction generates 24 and the product generated from the oxidation of 24 in acetone/TBAB/TBAAc. The cumulative data obtained from the electrochemical and chemical reactions confirm that the source of chloride is CH_2Cl_2 . A product analogous to that obtained from the oxidation of 24 in the acetone medium has also been obtained for 26. The cyclic voltammogram of 26 in a CH_2Cl_2 solution containing 0.1 M TBAB and excess TBAAc exhibits an anodic wave at +0.160 V, and a cathodic wave at -0.980 V. Controlled-potential coulometry at +0.250 V indicates that 26 undergoes a two-electron oxidation. The cyclic voltammogram of the oxidized solution exhibits a cathodic wave at -1.12 V with the anodic response at +0.115 V. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of the oxidized solution reveals a symmetrical pattern with a chemical shift and $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 16.4 ppm and 97.7 Hz, respectively. The $^{31}\text{P}\{\text{H}\}$ NMR data obtained from the oxidized solution is not identical to 42; however, the acetate-induced disproportionation reaction of 36 in CH_2Cl_2 generates 26, 42 and an unidentified compound. The difference in the product obtained when 26 is oxidized in a CH_2Cl_2 solution containing excess acetate and that obtained from the disproportionation reaction is unclear and requires further investigation.

The cyclic voltammetric behavior of 28 in a CH_2Cl_2 solution containing 0.1 M TBAN reveals two anodic waves at +0.106 V and +0.280 V, and three corresponding cathodic waves at +0.110, -0.003 and -0.711 V (Figure 38A). Controlled-potential coulometry at +0.40 V indicates that 28 undergoes a two-electron oxidation. The cyclic

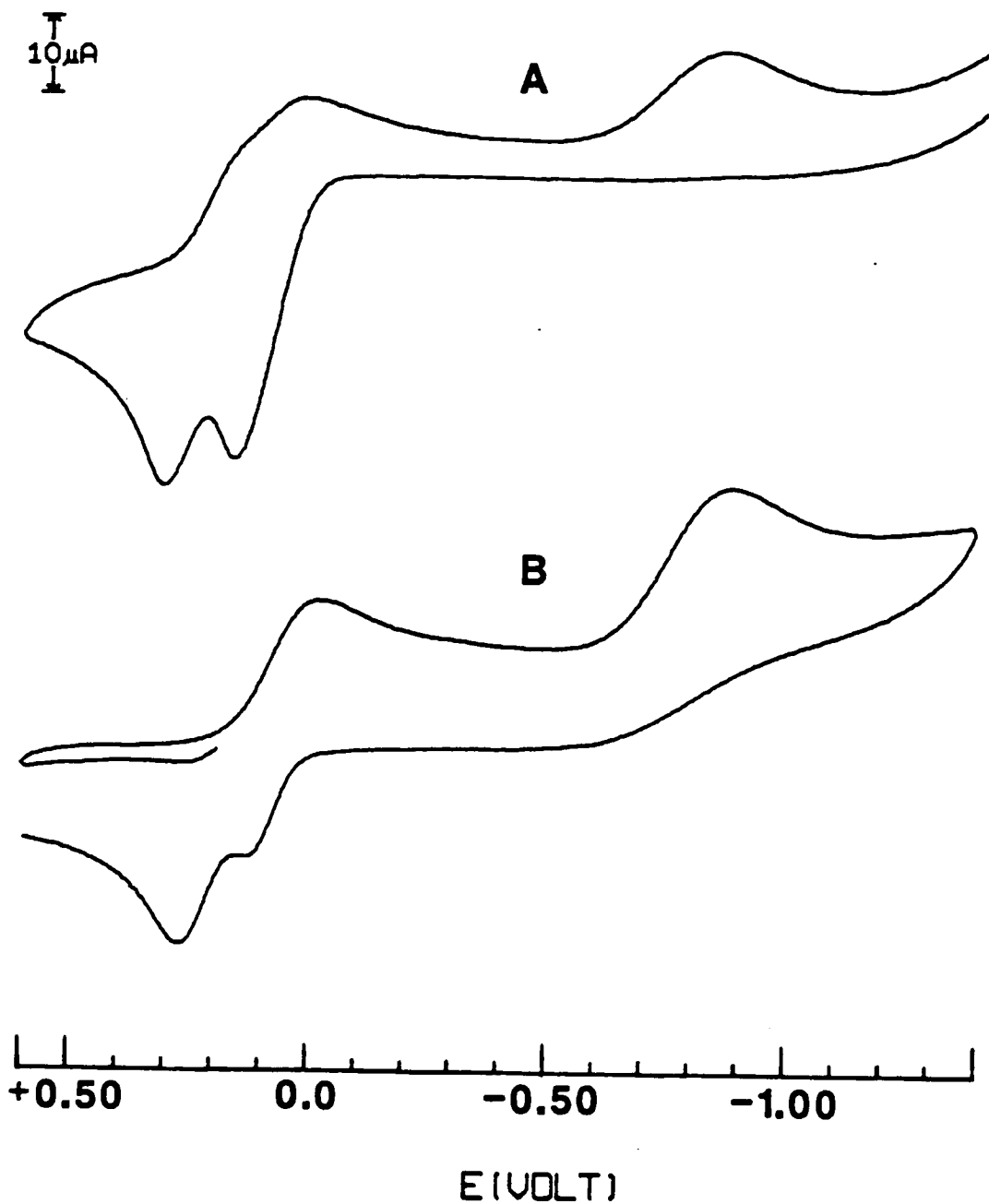


Figure 38. Cyclic voltammograms of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4B35MPz})](\text{PF}_6)$, 28, in $\text{CH}_2\text{Cl}_2/0.1$ M TBAN (A) before oxidation, and (B) after oxidation.

voltammogram of the oxidized solution exhibits two cathodic waves at -0.051 and -0.765 V with the anodic responses at +0.080 and +0.247 V (Figure 38B). The $^{31}\text{P(H)}$ NMR spectrum of the orange oxidized solution reveals a symmetrical pattern indicative of trans-dppm dinuclear rhodium complexes plus additional phosphorus resonances resulting from side products. The dinuclear Rh(II) species generated from the oxidation of 28 in a TBAN/ CH_2Cl_2 solution exhibits a chemical shift and $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 15.05 ppm and 92.8 Hz, respectively. The addition of nitrate ions to 34 does not result in a disproportionation reaction since the $^{31}\text{P(H)}$ NMR spectrum reveals only one phosphorus-containing dinuclear rhodium species. This species exhibits a symmetrical AA'A'A''XX' pattern with a chemical shift and $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 16.3 ppm and 92.8 Hz, respectively. These data are consistent with a Rh(II)-Rh(II) dimer.

The cyclic voltammetric behavior of 25 in the presence of ClO_4^- is similar to that obtained in the absence of a coordinating species. The cyclic voltammogram of 25 in a CH_2Cl_2 solution containing 0.1 M TBAH and excess ClO_4^- exhibits two anodic waves at +0.13 and +1.02 V, and two corresponding cathodic waves at +0.675 and +0.009 V (Figure 39A). Controlled-potential coulometry at +0.250 V indicates that 25 undergoes a one-electron oxidation. The cyclic voltammogram of the one-electron oxidized solution exhibits an anodic wave at +0.099 and +1.1 V, and two cathodic waves (Figure 39B). The cathodic wave that corresponds to the removal of the second electron occurs as a broad wave at approximately +0.500 V.

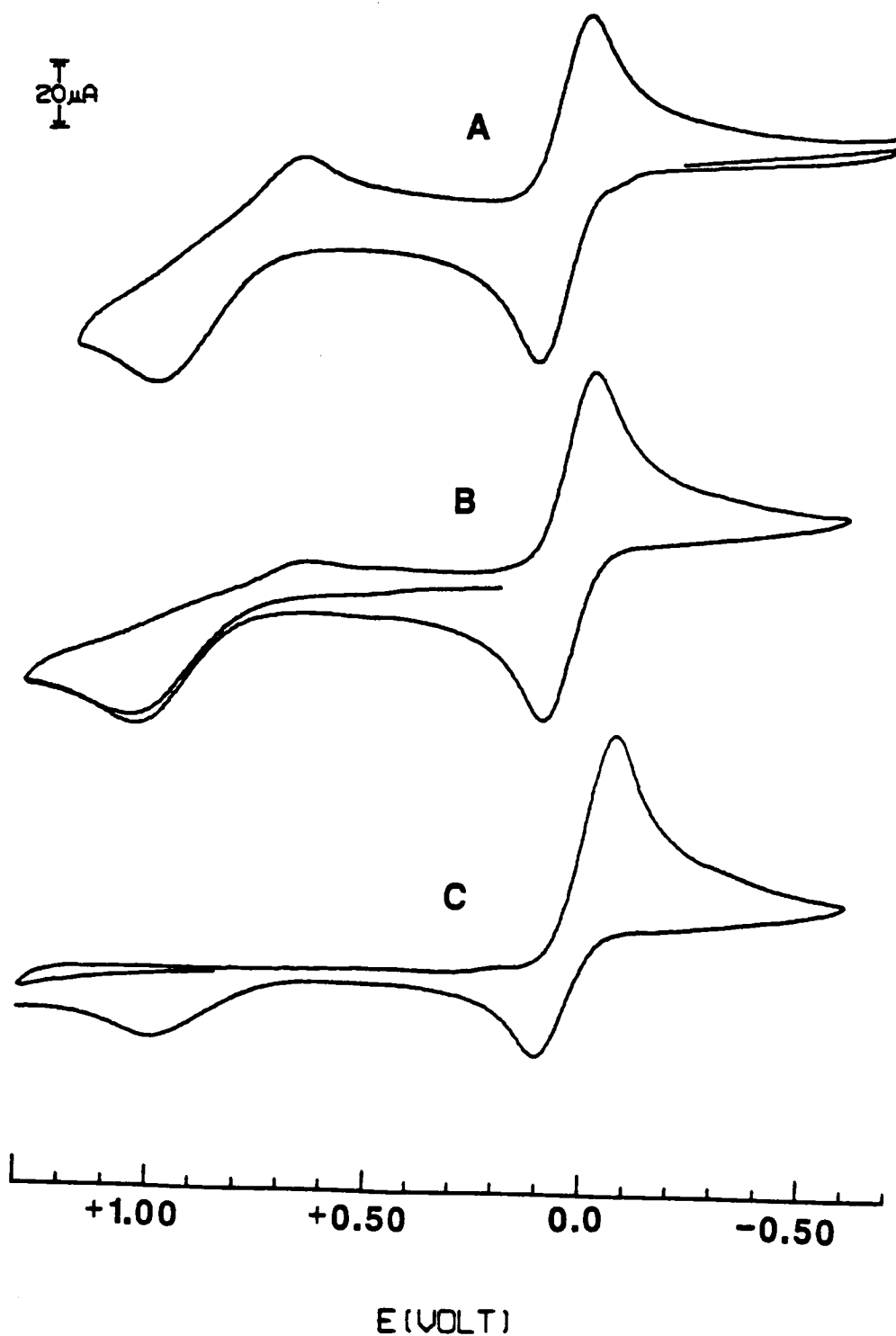


Figure 39. Cyclic voltammograms of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)$, 25, in $\text{CH}_2\text{Cl}_2/0.1$ M TBAH and 5.0×10^{-4} M TEAP (A) before oxidation, (B) after a one-electron oxidation, and (C) after a two-electron oxidation.

The cathodic wave corresponding to the first oxidation wave occurs at -0.015 V. Controlled-potential coulometry at +1.2 V indicates the removal of a second electron from 25. The cyclic voltammogram of the two-electron oxidized solution exhibits one cathodic wave at -0.956 V, and two anodic waves at +0.099 and +0.992 V (Figure 39C). Cycling the potential to a more negative potential reveals low-current cathodic and anodic waves at -0.850 and -0.200 V, respectively. Similar cyclic voltammetric behavior is observed for 25 in a CH₂Cl₂ solution saturated with TEAP.

The ³¹P{H} NMR spectrum of 25 in the oxidized CH₂Cl₂/TEAP solution reveals numerous phosphorus resonances. The addition of ClO₄⁻ to a CH₂Cl₂ solution of 34 results in no reaction. The absence of a reaction is not surprising since perchlorate has only a limited tendency to serve as a coordinating ligand.^{101,103}

The cyclic voltammetric behavior of dinuclear Rh(I) compounds in the presence of acetate, nitrate and perchlorate indicates that the coordinating ability of these compounds is in the order: acetate > nitrate > perchlorate. In the presence of acetate, the cyclic voltammogram of 26 reveals a totally irreversible process with the simultaneous removal of both electrons. The cyclic voltammogram of 25 in the presence of perchlorate, before electrolysis, results in a small change from that observed for 25 in a CH₂Cl₂/TBAH solution. In the presence of nitrate, the cyclic voltammetric behavior of 24 is between that observed for 26 in the presence of acetate and that of 25 in a perchlorate solution.

The cyclic voltammetric behavior of 18-20, 21 and 22 in the

coordinating solvent, CH_3CN , exhibits one two-electron couple with $E_{1/2}$ values between +0.473 and +0.534 V, and an irreversible cathodic wave in the range of -1.4 to -1.7 V (Table VI, page 156). A typical cyclic voltammogram in CH_3CN is illustrated in Figure 40 by 23. The cyclic voltammogram exhibits an anodic wave at 0.604 V with the corresponding cathodic responses at +0.472, +0.19 and -0.158 V. Cycling the potential in the negative direction reveals an irreversible cathodic wave at -1.410 V with anodic responses at -0.158 and -0.611 V. Analysis of the cyclic voltammetric data for the two-electron couple is given in Table XVIII, and indicates the following: (1) the potential separations, ΔE , between the anodic and cathodic peak potentials were in all cases greater than 0.060 V, and increased with scan rate, (2) the half-wave potentials, $E_{1/2}$, were invariant with scan rate, except for 20, and (3) the ratios of the peak currents, i_{pc}/i_{pa} , are approximately unity for 18 and 22; 0.7 for 20; and the ratio for 19 and 23 varies over the range of sweep rates. The cyclic voltammetric behavior for 18 and 22 are consistent with a quasi-reversible couple.⁸⁷⁻⁸⁹

Unlike the cyclic voltammetric behavior in CH_2Cl_2 , compounds 18-20, 22 and 23 exhibit an irreversible reduction wave well within the negative potential limit of CH_3CN . Compound 23 was chosen to investigate the reduction wave for comparison to its electrochemical behavior in CH_2Cl_2 . The cyclic voltammogram of 23 in a CH_3CN solution containing 0.1 M TBAH is shown in Figure 40. Controlled-potential coulometry at -1.50 V indicates that 23 undergoes a two-electron reduction generating a dinuclear Rh(0) compound. The

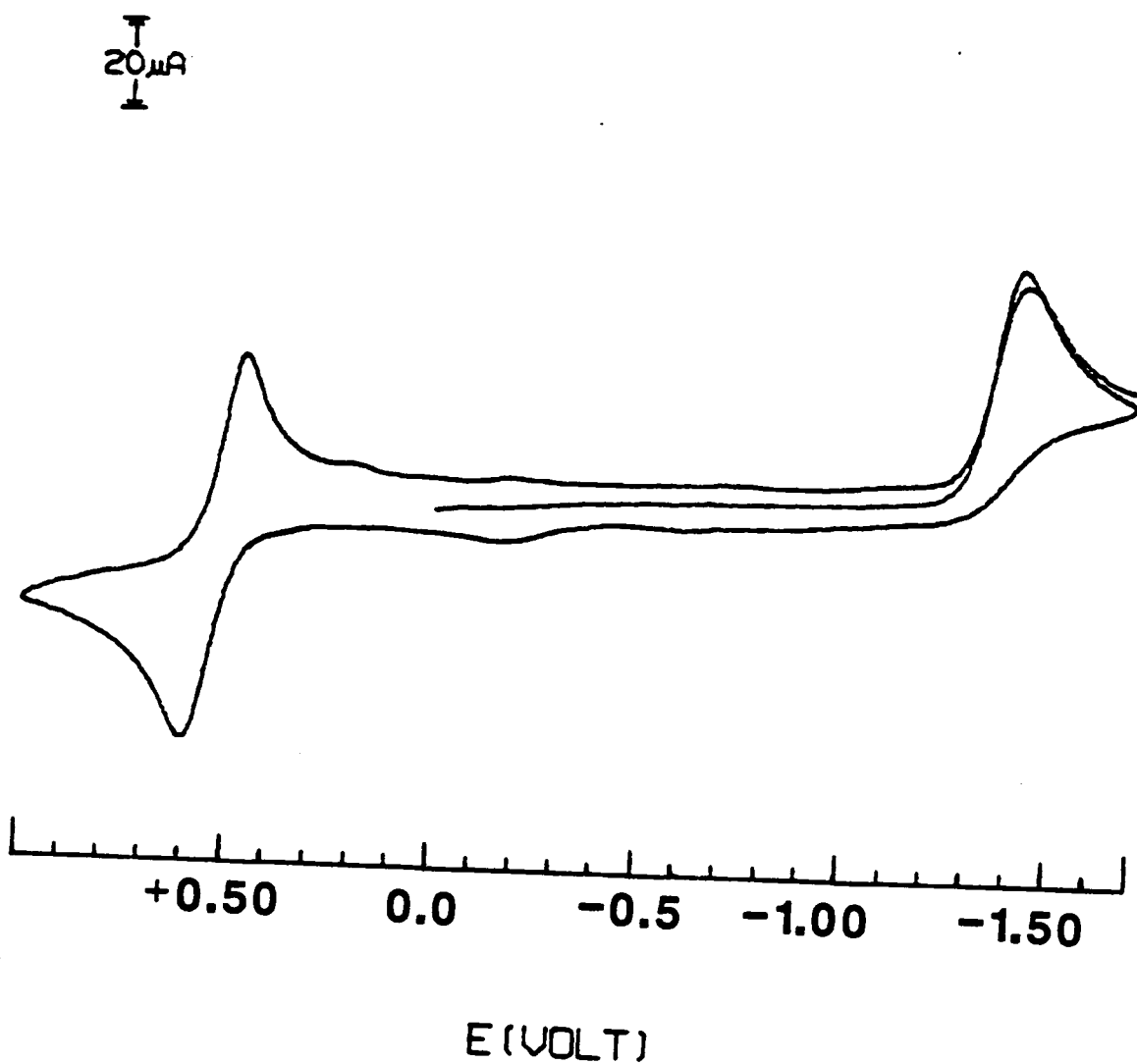


Figure 40. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-345BPz})](\text{PF}_6)$, 23, in 0.1 M TBAH/ CH_3CN .

TABLE XVIII

CYCLIC VOLTAMMETRIC DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-Z})](\text{PF}_6)$ IN CH_3CN

Z	v^a	E_{pa} , V	E_{pc} , V	ΔE , V	$E_{1/2}$, V	i_{pc}/i_{pa}
Pz, <u>18</u>	50	0.515	0.423	0.092	0.469	1.1
	100	0.516	0.424	0.092	0.470	1.1
	200	0.526	0.419	0.107	0.472	1.0
	300	0.539	0.395	0.144	0.467	0.9
	400	0.540	0.400	0.140	0.470	0.9
	500	0.545	0.401	0.144	0.473	0.9
35MPz, <u>19</u>	50	0.532	0.415	0.117	0.474	1.0
	100	0.547	0.397	0.150	0.472	1.0
	200	0.566	0.380	0.186	0.473	0.9
	300	0.581	0.365	0.216	0.473	0.7
	400	0.587	0.363	0.224	0.475	0.7
	500	0.600	0.354	0.246	0.477	0.5
4MPz, <u>20</u>	50	0.525	0.348	0.176	0.436	0.7
	100	0.539	0.338	0.201	0.438	0.7
	200	0.548	0.330	0.212	0.439	0.7
	300	0.561	0.324	0.237	0.442	0.7
	400	0.574	0.307	0.267	0.440	0.7
	500	0.592	0.300	0.292	0.446	0.7
4B35MPz, <u>22</u>	50	0.506	0.439	0.067	0.472	1.0
	100	0.509	0.438	0.071	0.474	1.0
	200	0.523	0.429	0.094	0.476	1.0
	300	0.532	0.423	0.109	0.478	1.0
	400	0.546	0.403	0.143	0.474	1.0
	500	0.544	0.412	0.132	0.478	1.0
345BPz, <u>23</u>	50	0.574	0.485	0.090	0.530	0.88
	100	0.588	0.479	0.109	0.534	0.88
	200	0.599	0.472	0.127	0.536	0.78
	300	0.605	0.465	0.140	0.535	0.74
	400	0.615	0.464	0.151	0.540	0.69
	500	0.629	0.444	0.185	0.537	0.54

^a Scan rate in mV/s

cyclic voltammogram of the resulting reduction reveals anodic waves at +0.52, -0.03, -0.473 and -1.496 V. Controlled-potential coulometry at +0.65 V of the electrolysis solution indicates a two-electron oxidation. The cyclic voltammogram reveals cathodic waves at +0.457, -0.461, -0.848, and -1.466 V, and anodic waves at -0.59, -0.25, +0.028, +0.208, and +0.580 V. The $E_{1/2}$ value of +0.123 V obtained from the cyclic voltammogram indicates that 23 might have been regenerated. The $^{31}\text{P(H)}$ NMR spectrum of the isolated product exhibits a symmetrical pattern centered at 20.64 ppm (Figure 41).

The observed $^{31}\text{P(H)}$ NMR pattern is not the pattern observed for 23 or any of the dicarbonyl-pyrazolate complexes. The chemical shift does indicate that it is a dinuclear Rh(I) compound. The observed pattern could be a result of a structural rearrangement of the bridging dppm ligands possibly to a cis orientation or the presence of two different compounds. The IR spectrum indicates terminal carbonyl ligands with CO stretching frequencies of 1990(s) and 1975(s) cm^{-1} , indicative of 23. This is in contrast with the electrochemical behavior of 23 in CH_2Cl_2 . In CH_2Cl_2 , reduction at -1.579 V appears to involve the solvent. Also, after bulk reduction in CH_2Cl_2 , 23 undergoes an irreversible change as determined by the cyclic voltammogram after bulk oxidation. Another dissimilarity between the electrochemical behavior of the dicarbonyl species in $\text{CH}_2\text{Cl}_2/\text{TBAH}$ and its electrochemical behavior in $\text{TBAH}/\text{CH}_3\text{CN}$ is the different cyclic voltammograms obtained before and after bulk oxidation. The cyclic voltammogram of 22 in a CH_3CN

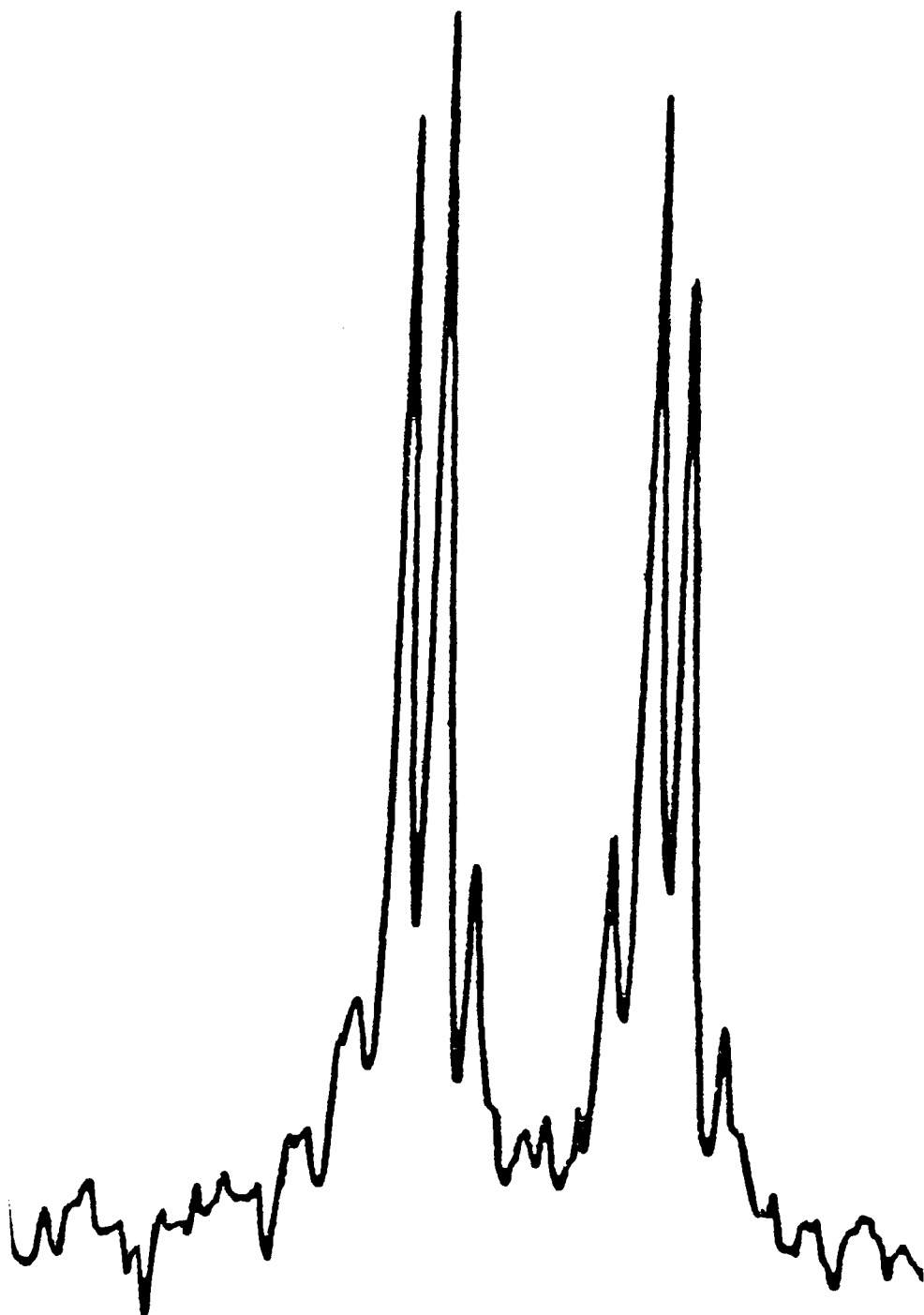


Figure 41. $^{31}\text{P}\{\text{H}\}$ NMR spectrum of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-345BPz})](\text{PF}_6)$, 23, that was reduced by two electrons, then oxidized by two electrons in $\text{CH}_3\text{CN/TBAH}$.

solution containing 0.1 M TBAB reveals a single anodic wave at +0.516 V, and two cathodic responses +0.435 and +0.160 V (Figure 42A). Controlled-potential coulometry at +0.600 V indicates a two-electron oxidation. The cyclic voltammogram of the oxidized solution exhibits two one-electron couples with cathodic waves at +0.404 and +0.106 V, and two corresponding anodic waves at +0.522 and +0.162 V, respectively (Figure 42B). The $^{31}\text{P}(\text{H})$ NMR spectrum of the oxidized solution exhibits an AA'A''A'''XX' symmetrical pattern with a chemical shift of 14.5 ppm and a $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 75.7 Hz. These values are indicative of a dirhodium(II) complex. The cyclic voltammogram after obtaining the NMR spectrum reveals an additional cathodic wave at -0.216 V (Figure 42C). A normal pulse voltammogram, shown in Figure 43, reveals the presence of three waves with half-wave potentials at +0.392, -0.108 and -0.200 V. The total current consumed for the first wave equals that of the other two combined, $1.7 \times 10^{-4} \mu\text{A}$ and $1.8 \times 10^{-4} \mu\text{A}$, respectively. It will be shown later, by NMR spectroscopy, that the complex that gives rise to the half-wave potential at +0.108 V also generates the half-wave potential at -0.20 V. Controlled-potential coulometry at +0.350 V indicates a one-electron reduction. The cyclic voltammogram of the one-electron reduced solution exhibits three cathodic waves at +0.419, +0.104 and -0.206 V, and two anodic waves at +0.530 and +0.165 V. The $^{31}\text{P}(\text{H})$ NMR spectrum on the one-electron reduced solution indicates the presence of two species both exhibiting a symmetrical AA'A''A'''XX' pattern. The chemical shifts of the products obtained from the one-electron reduction are 23.3

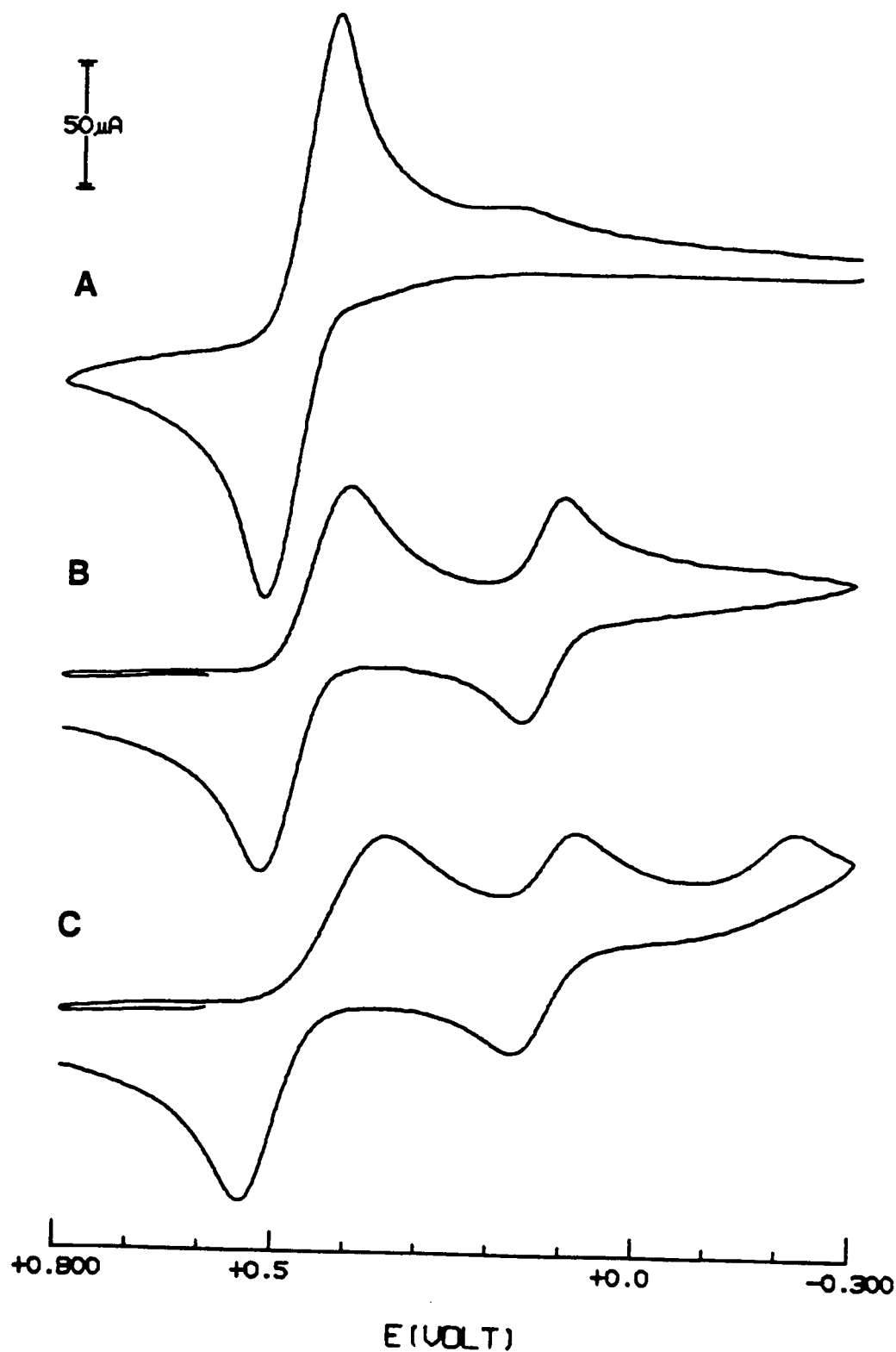


Figure 42. Cyclic voltammograms of 10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4B35MPz})](\text{PF}_6)$, **22**, in $\text{CH}_3\text{CN}/0.1$ M TBAB (A) before oxidation, (B) after oxidation, and (C) after oxidation and the acquisition of a NMR spectrum.

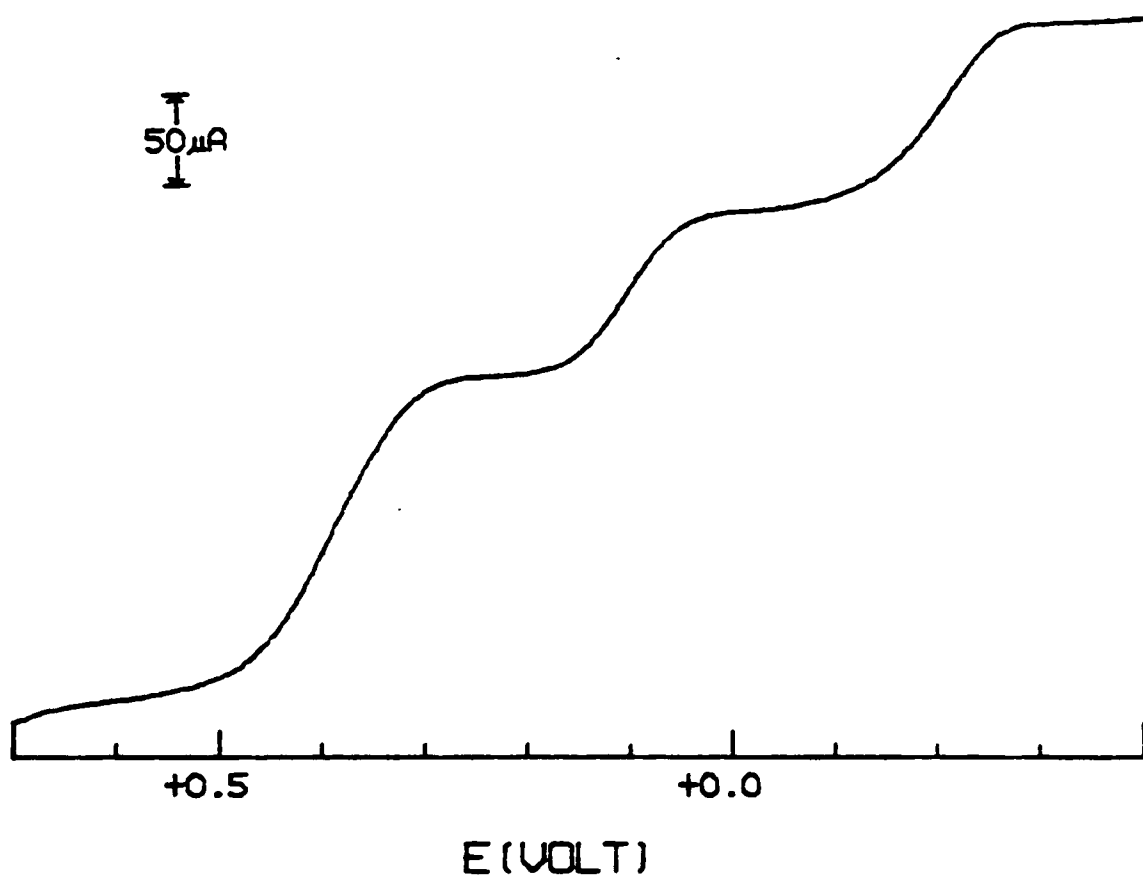


Figure 43. Normal pulse voltammogram of 10^{-4} $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2(\mu\text{-4B35MPz})](\text{PF}_6)_3$, 22, in 0.1 M TBAB/ CH_3CN .

and 10.6 ppm, with [$^1J_{\text{(Rh-P)}} + ^xJ_{\text{(Rh-P)}}$] values of 126.9 and 104.2 Hz, respectively. These values are consistent with a Rh(I) and Rh(II) dimer. The species exhibiting a chemical shift and [$^1J_{\text{(Rh-P)}} + ^xJ_{\text{(Rh-P)}}$] value of 23.3 ppm and 126.9 Hz, respectively, are identical to those observed for 22. The formation of a Rh(I) and Rh(II) dimer indicates an EC mechanism; that is, a disproportionation reaction following the electrochemical one-electron reduction. The one-electron reduction presumably generates a Rh(1.5) dimer, which in the presence of CH_3CN , a coordinating solvent, disproportionates to produce a Rh(I) and Rh(II) dimer. Exhaustive bulk electrolysis at +0.050 V results in the cyclic voltammogram exhibiting three cathodic waves at +0.398, +0.102 and -0.241 V, and two anodic waves at +0.180 and +0.565 V. The $^{31}\text{P(H)}$ NMR spectrum reveals the presence of the same two species obtained from the reduction at +0.350 V; however, the Rh(II) dimer is diminished by approximately 75%. Further bulk reduction at -0.300 V results in the total loss of the Rh(II) dimer as determined by the $^{31}\text{P(H)}$ NMR spectrum. The cyclic voltammogram of the reduced solution before obtaining the NMR spectrum reveals two anodic waves at +0.205 and +0.612 V with two cathodic responses at +0.080 and +0.346 V, respectively. After obtaining the $^{31}\text{P(H)}$ NMR spectrum, the cyclic voltammogram reveals only one anodic wave at +0.565 V, and one cathodic response at +0.424 V. The loss of the Rh(II) dimer after reduction at -0.300 V demonstrates that the two half-wave potentials observed in the normal pulse voltammogram at +0.108 and -0.200 V are related to the same species. The differences between the Rh(II)

dimer generated from the initial two-electron oxidation and the Rh(II) dimer generated from the disproportionation reaction have not been determined.

The addition of two equivalents of I^- to a solution of 18 that was oxidized at +0.55 V in a CH_3CN solution containing 0.1 M TBAH generates the diiodo complex by displacing coordinated CH_3CN . The $^{31}P(H)$ NMR spectrum of the isolated product exhibits an AA'A''A'''XX' pattern with a chemical shift of 4.8 ppm and a $[^1J_{(Rh-P)} + ^xJ_{(Rh-P)}]$ value of 83.0 Hz. The IR spectrum indicates the presence of terminal carbonyl ligands with stretching frequencies of 2054(s) and 2023(m) cm^{-1} , and the presence of PF_6^- at 839(s) and 557(m) cm^{-1} . These data are identical to an authentic sample of $[Rh_2(\mu-dppm)_2(CO)_2I_2(\mu-Pz)](PF_6)$.⁸¹

The cyclic voltammograms of 24-26, 28 and 29 in CH_3CN reveal a coalescence of the two anodic waves observed in CH_2Cl_2 , resulting in a single two-electron couple with an $E_{1/2}$ value of approximately 0.042 V. A typical cyclic voltammogram in CH_3CN is illustrated by 28 in Figure 44A. It exhibits anodic waves at -0.01 and +0.113 V, and a corresponding cathodic wave at +0.033 V. Analysis of the cyclic voltammetric data for 24-26, 28 and 29 is given in Table XIX, and indicates the following: (1) the potential separations, ΔE , between the anodic and cathodic peak potentials were in all cases greater than 0.070 V, and increased with scan rate, (2) the half-wave potentials, $E_{1/2}$, were invariant with scan rate, and (3) the ratios of the peak currents, i_{pc}/i_{pa} , were greater than 1.0. This behavior is consistent with a two-electron quasi-reversible

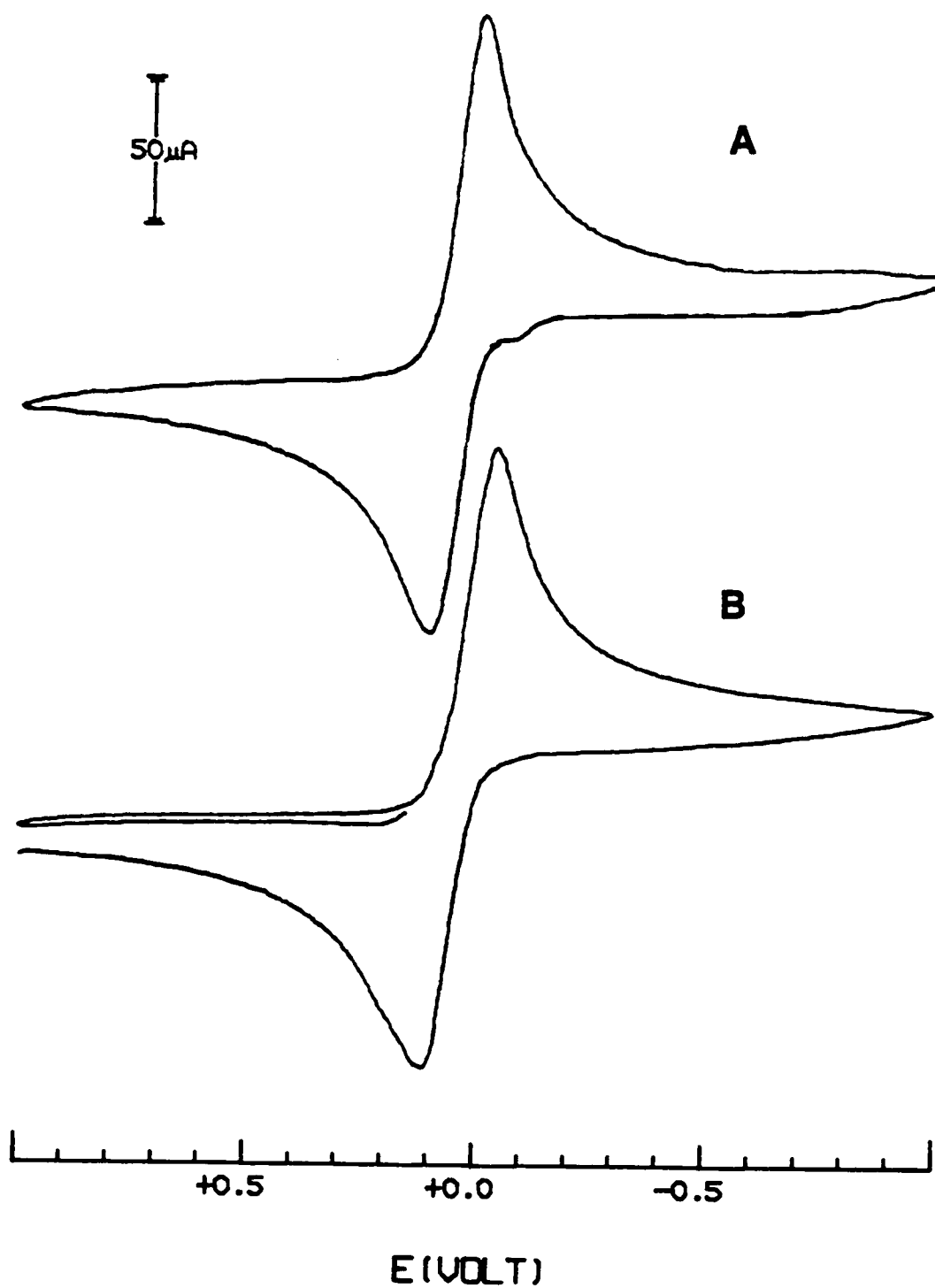


Figure 44. Cyclic voltammograms of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4B35MPz})](\text{PF}_6)$, **28**, in $\text{CH}_3\text{CN}/0.1$ M TBAB (A) before oxidation, and (B) after oxidation.

TABLE XIX

CYCLIC VOLTAMMETRIC DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-Z})](\text{PF}_6)$ IN CH_3CN

Z	v^a	E_{pa} , V	E_{pc} , V	ΔE , V	$E_{1/2}$, V	i_{pc}/i_{pa}
Pz, <u>24</u>	50	0.067	-0.022	0.089	0.023	1.2
	100	0.068	-0.025	0.093	0.022	1.3
	200	0.076	-0.029	0.105	0.024	1.3
	300	0.080	-0.034	0.114	0.023	1.4
	400	0.086	-0.039	0.125	0.024	1.4
	500	0.089	-0.044	0.133	0.023	1.5
4MPz, <u>25</u>	50	0.039	-0.055	0.094	-0.008	1.3
	100	0.046	-0.057	0.103	-0.006	1.3
	200	0.054	-0.070	0.124	-0.008	1.4
	300	0.062	-0.077	0.139	-0.008	1.5
	400	0.071	-0.086	0.157	-0.008	1.6
	500	0.077	-0.092	0.169	-0.008	1.7
35MPz, <u>26</u>	50	0.069	-0.026	0.095	0.022	1.2
	100	0.078	-0.030	0.108	0.024	1.5
	200	0.083	-0.036	0.119	0.024	1.6
	300	0.086	-0.042	0.128	0.022	1.6
	400	0.099	-0.044	0.143	0.028	1.7
	500	0.102	-0.052	0.154	0.025	1.9
4B35MPz, <u>28</u>	50	0.115	0.023	0.092	0.069	1.3
	100	0.125	0.016	0.109	0.071	1.4
	200	0.133	0.005	0.128	0.069	1.5
	300	0.135	-0.017	0.152	0.059	1.5
	400	0.135	-0.028	0.163	0.054	1.4
	500	0.141	-0.029	0.170	0.056	1.4
345BPz, <u>29</u>	50	0.140	0.061	0.079	0.101	1.0
	100	0.149	0.052	0.097	0.101	1.0
	200	0.157	0.042	0.115	0.100	1.1
	300	0.167	0.031	0.136	0.099	1.1
	400	0.174	0.024	0.150	0.099	1.1
	500	0.174	0.024	0.150	0.099	1.1

^a Sweep rate in mV/s

couple,⁸⁷⁻⁸⁹ except for the observed current ratio. The increase in the current ratio arises from a decrease in the anodic peak current. For 24-26, the decrease in the anodic peak current as the scan rate increases results from a broadening of the anodic wave.

The addition of increasing amounts of CH_3CN to a CH_2Cl_2 solution containing 0.1 M TBAH and 25 results in a shift of the second anodic wave to less-positive potentials. Figure 45 shows differential pulse voltammograms of 25 in the presence of 0.0, 1.0, 4.0, 8.0 and 20.0 equivalents of CH_3CN . The differential pulse voltammograms reveal a decrease in current at +1.03 V and a simultaneous increase in current at +0.460 V as the amount of CH_3CN increases. Figure 45 also shows that the first anodic wave at +0.036 V is independent of the amount of CH_3CN added. This behavior demonstrates that CH_3CN is facilitating the removal of the second electron, and not affecting the removal of the first electron. Further investigation into the high $i_{\text{pc}}/i_{\text{pa}}$ ratio relates the effect of increasing scan rate on the cyclic voltammetric behavior of 25 in a CH_3CN solution containing 0.1 M TBAH. The cyclic voltammograms reveal that as the scan rate is increased from 0.1 to 10 V/s, the anodic wave first broadens and then develops into two overlapping waves with the retainment of a single cathodic wave (Figure 46). This is further evidence indicating that CH_3CN is interacting with the one-electron oxidized species, and facilitating the removal of the second electron. At slow scan rates, the reaction rate of the interaction of CH_3CN with the mixed-valence species is greater than the time scale of the cyclic voltammogram, and a single anodic wave results. At a scan

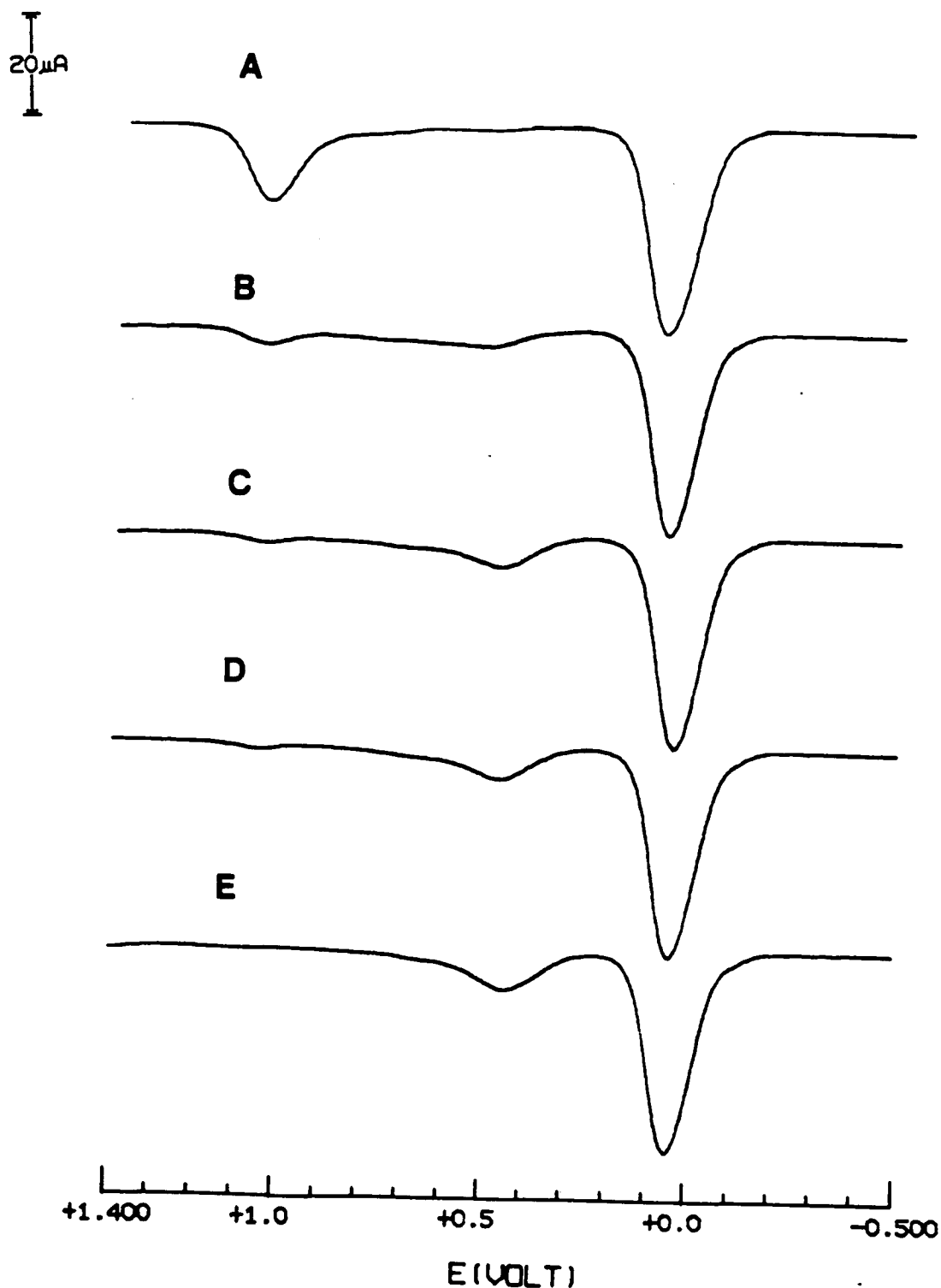


Figure 45. Differential pulse voltammograms of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)$, 25, in $\text{CH}_2\text{Cl}_2/0.1 \text{ M TBAH}$ and (A) 0.0, (B) 1.0, (C) 4.0, (D) 8.0, and (E) 20.0 equivalents of CH_3CN .

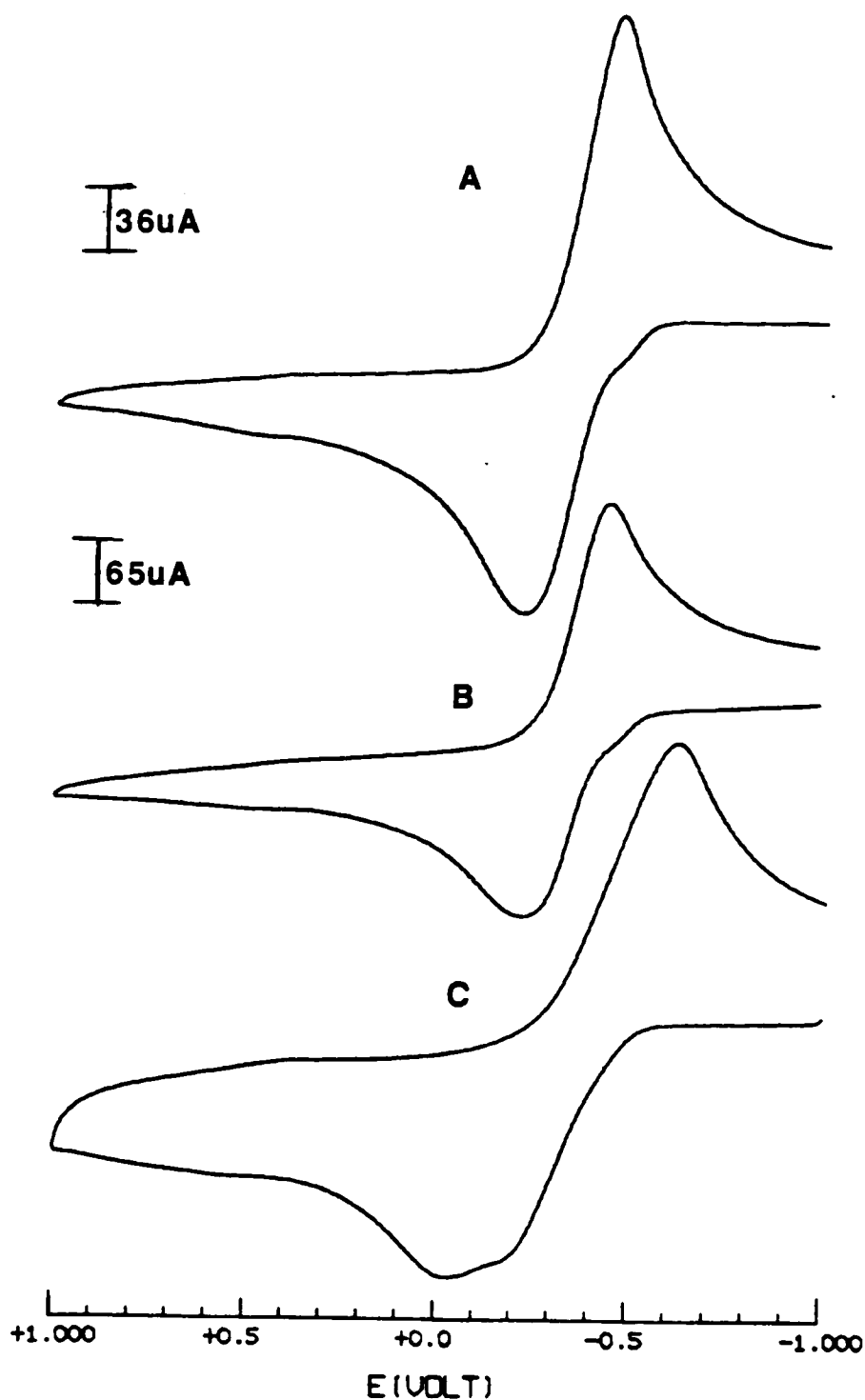


Figure 46. Cyclic voltammograms of 10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)$, 25, in $\text{CH}_3\text{CN}/0.1$ M TBAH at potential sweep rates of (A) 0.50, (B) 1.0, and (C) 10.0 V/s.

rate of 10 V/s, the time scale of the cyclic voltammogram is greater than the rate of reaction of CH_3CN with the mixed-valence species, and two anodic waves appear. This behavior of 25 with CH_3CN results in the observed increase of the current ratio, $i_{\text{pc}}/i_{\text{pa}}$, as the scan rate increases. Since the anodic wave is broad at higher scan rates, a lower value for the anodic peak current versus the cathodic current occurs resulting in an increase in the current ratio value. This explains the increase in the current ratio as the scan rate increases for 24-26.

The difference in the electrochemical behavior of a dicarbonyl and a diisocyanide complex in CH_3CN is observed in the cyclic voltammogram after a two-electron bulk oxidation. As observed with 22, the cyclic voltammograms before and after bulk electrolysis are different. For 28, a diisocyanide complex, the cyclic voltammograms before and after bulk oxidation are similar. The cyclic voltammogram of a CH_3CN solution containing 0.1 M TBAB and 28 exhibits anodic waves at -0.01 and +0.113 V, and a cathodic wave at -0.033 V (Figure 44A). Controlled-potential coulometry at +0.200 V indicates that 28 undergoes a two-electron process. The cyclic voltammogram of the oxidized solution exhibits a cathodic wave at -0.050 V, with the anodic response at +0.112 V (Figure 44B). Similar cyclic voltammograms obtained before and after bulk electrolysis indicate that the product generated on the time scale of a cyclic voltammogram and that obtained on the bulk electrolysis time scale are similar. The $^{31}\text{P}(\text{H})$ NMR spectrum of the oxidized solution exhibits an AA'A'A''XX' pattern with a chemical shift and $[^1\text{J}_{(\text{Rh-P})} +$

$^xJ_{(\text{Rh-P})}$ value of 11.45 ppm and 85.4 Hz, respectively. The oxidized product of 28 in TBAB/ CH_3CN can also be generated by the addition of CH_3CN to 37; however, a disproportionation reaction does not occur, and only the Rh(II) dimer is produced.

The electrochemistry of 18-20, 22-26, 28 and 29 in the presence of CH_3CN and CH_2Cl_2 reveals that the electrochemical behavior of these compounds depends strongly on the solvent. In a non-coordinating solvent, CH_2Cl_2 , the cyclic voltammogram exhibits a one-electron quasi-reversible and a one-electron irreversible process. In a coordinating solvent, CH_3CN , the cyclic voltammogram exhibits a single two-electron process. It was concluded that CH_3CN facilitates the removal of the second electron, and stabilizes the dinuclear Rh(II) species. The cyclic voltammetric behavior in the CH_3CN solution lead to the electrochemical investigation of 25 in the presence of other neutral coordinating species; pyridine, 3,5-dimethylpyridine and 4-dimethyl-aminopyridine.

In the presence of pyridine, the second one-electron process shifts toward a less-positive potential with a simultaneous change toward a quasi-reversible electron-transfer process. The cyclic voltammograms of 25 in a CH_2Cl_2 solution containing 0.1 M TBAH in the presence of pyridine are shown in Figure 47. The addition of increasing amounts of pyridine results in a continual shift of the second anodic wave to less-positive potentials. The shift in the second anodic wave of 0.63 V from +1.142 to +0.512 V results after the addition of ten equivalents of pyridine. The cathodic response also demonstrates a decrease in potential from +0.681 to +0.263 V.

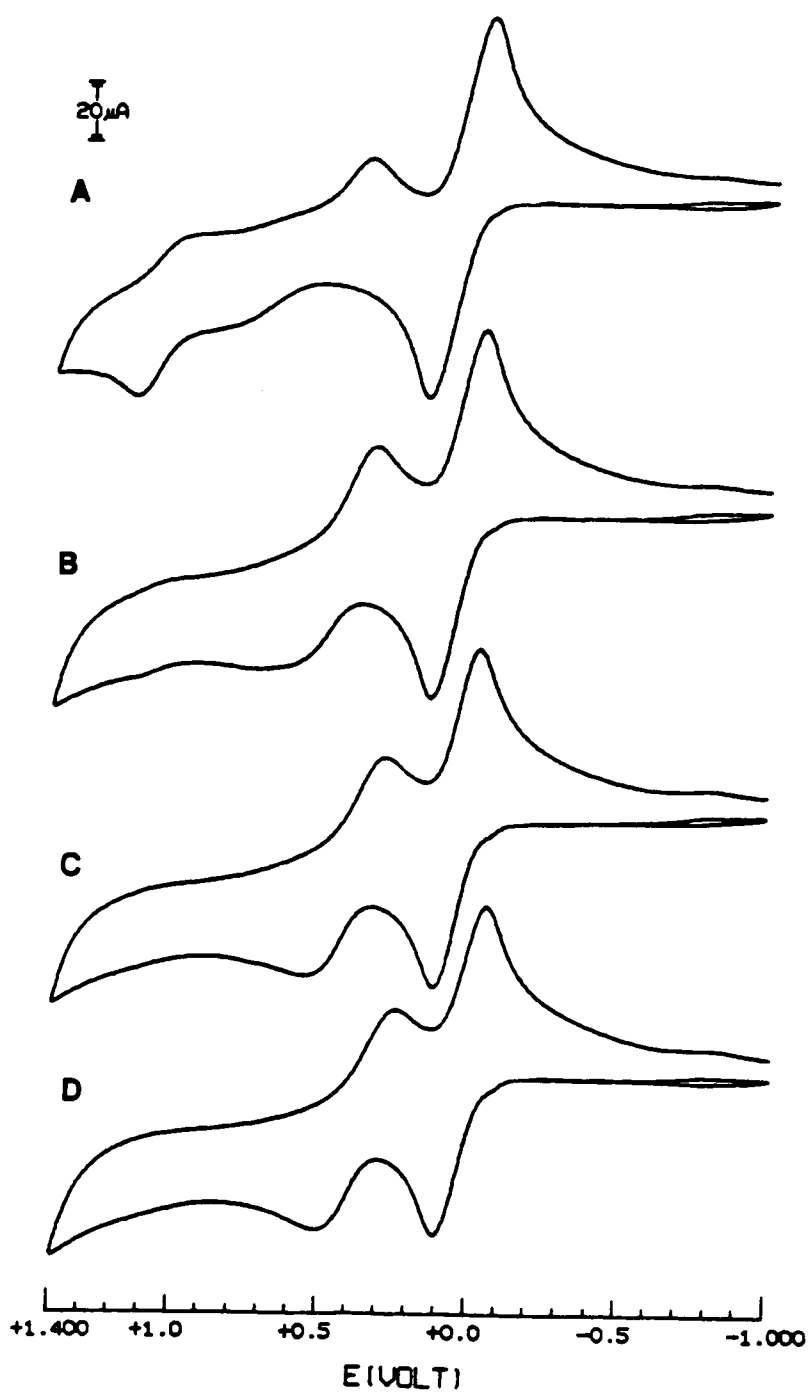


Figure 47. Cyclic voltammograms of 10^{-3} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)_3$, 25, in a CH_2Cl_2 solution containing 0.1 M TBAH and (A) 1.0, (B) 3.0, (C) 5.0, and (D) 10.0 equivalents of pyridine.

The effect of pyridine on the first one-electron couple is not as pronounced. A decrease in the $E_{1/2}$ value from +0.095 to +0.069 V occurs after the addition of ten equivalents of pyridine. The change in the oxidation potentials as a function of pyridine was also monitored by differential pulse voltammetry. The differential pulse voltammogram shown in Figure 48 reveals a decrease in the current at +1.036 V, and a simultaneous increase in an anodic wave at approximately +0.4 V as the amount of pyridine is increased. The differential pulse voltammogram also reveals an independence of the first anodic wave as a function of pyridine.

The cyclic voltammetric behavior of 25 in a CH_2Cl_2 solution containing 0.1 M TBAH in the presence of 3,5-dimethylpyridine is shown in Figure 49. The anodic wave of the second-electron process shows a similar decrease in potential that was demonstrated for pyridine. The addition of eight equivalents of 3,5-dimethylpyridine results in a shift of the second anodic wave to 0.442 V from 1.112 V. The cathodic response to the second anodic wave occurs at -0.033 V, which is the same potential as the cathodic response to the first anodic wave. The potential of the cathodic response demonstrates the irreversibility of the second-electron process at .100 V/s. When the scan rate is decreased to .010 V/s, what appears to be two quasi-reversible waves with $E_{1/2}$ values of +0.042 and +.308 V are observed (Figure 49D). Based on the cyclic voltammetric data, the complex generated after the removal of the second electron is easily reduced at slow-scan rates.

The cyclic voltammetric behavior of 25 in the presence of

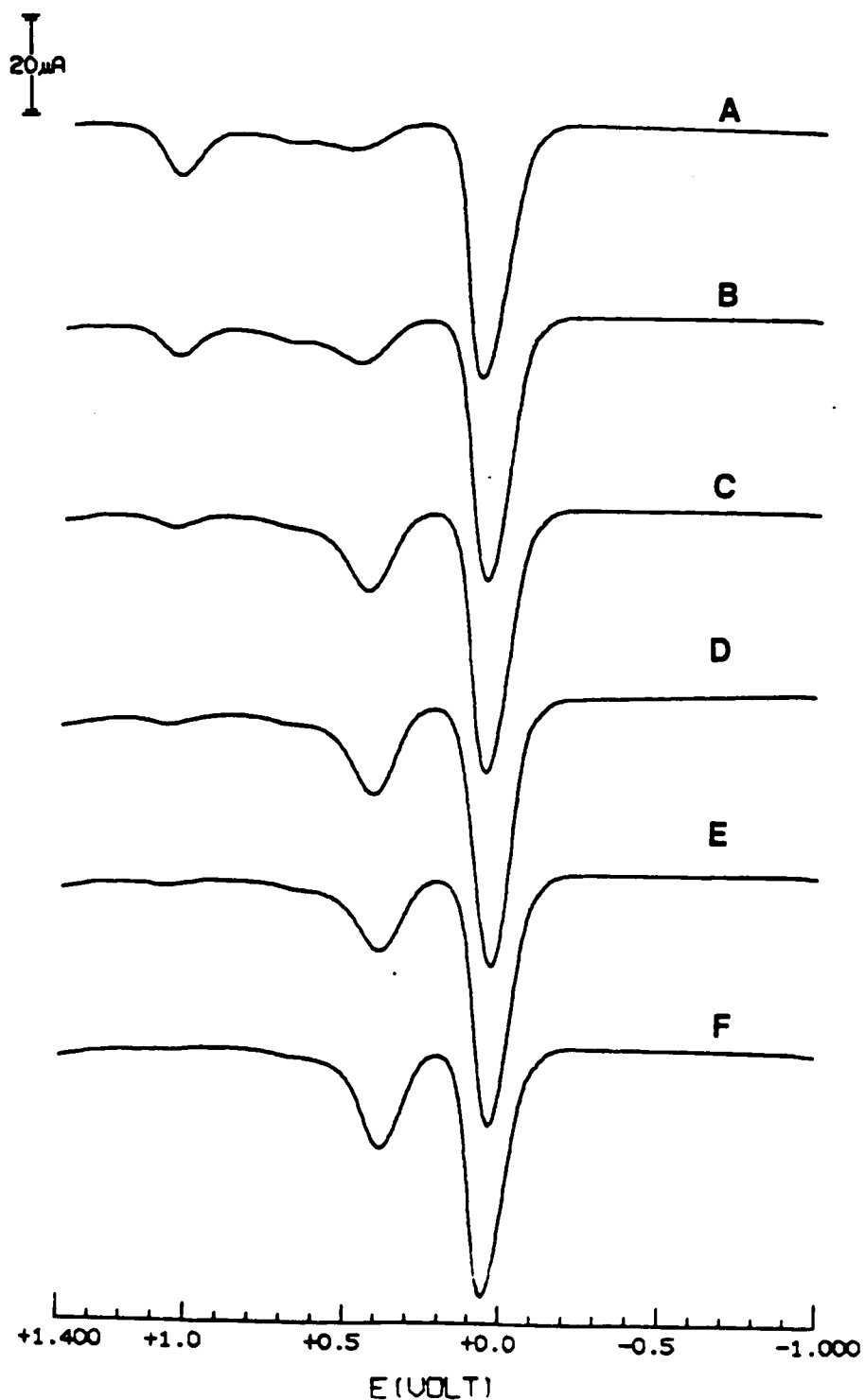


Figure 48. Differential pulse voltammograms of 10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)_2$, 25, in a CH_2Cl_2 solution containing 0.1 M TBAH and (A) 0.5, (B) 1.0, (C) 2.0, (D) 3.0, (E) 5.0, and (F) 10.0 equivalents of pyridine.

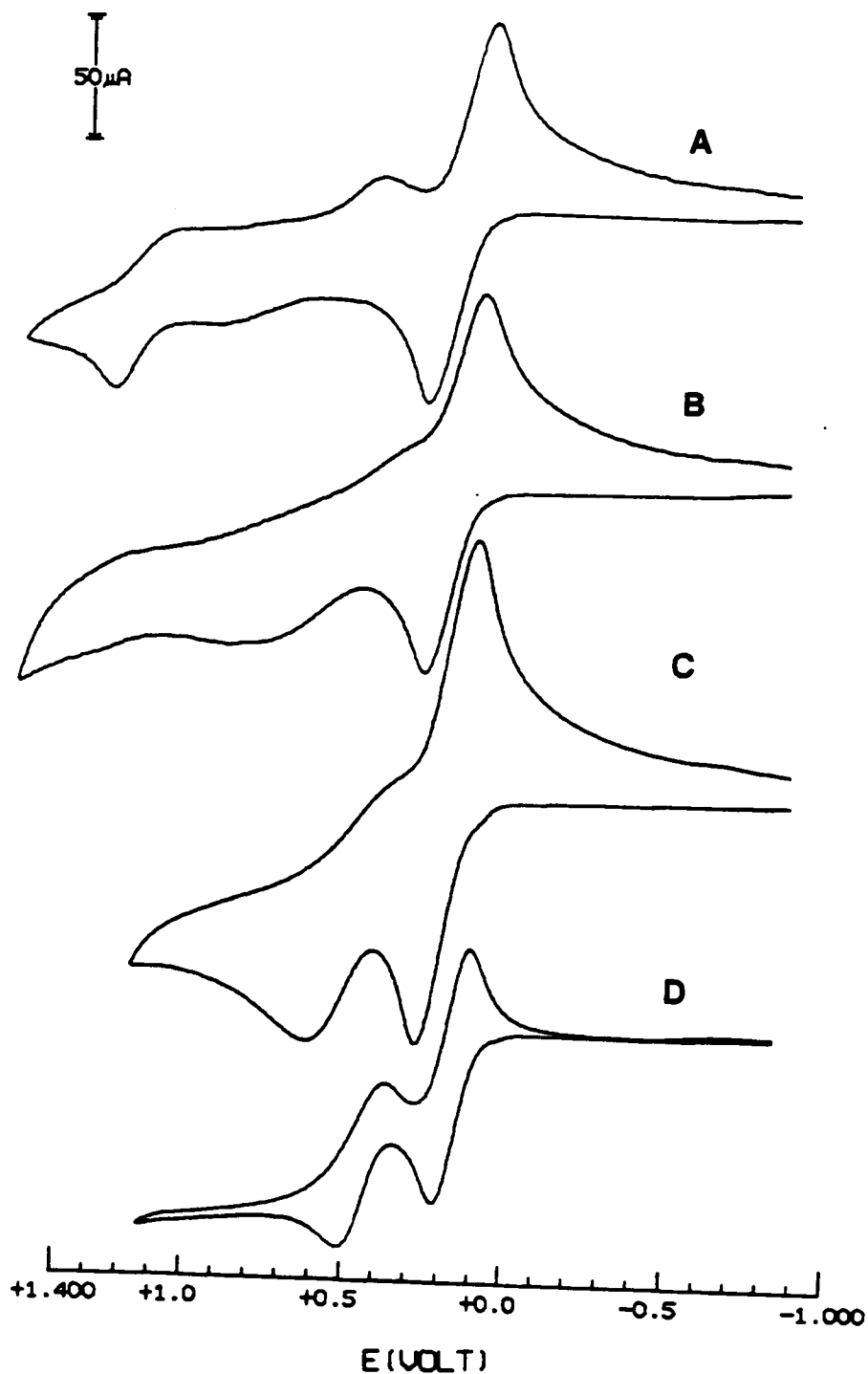


Figure 49. Cyclic voltammograms of 10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)$, 25, in a CH_2Cl_2 solution containing 0.1 M TBAH and (A) 0.5, (B) 2.0, (C) 8.0 equivalents of 3,5-dimethylpyridine at scan rate of 0.100 V/s and (D) 8.0 equivalents of 3-5-dimethylpyridine at scan rate of 0.010 V/s.

4-(dimethylamino)pyridine in a CH_2Cl_2 solution containing 0.1 M TBAH is shown in Figure 50. In the potential range, +1.6 to -1.6 V, the cyclic voltammogram of 4-(dimethylamino)pyridine exhibits an irreversible anodic wave at +1.26 V with the cathodic response at -1.33 V. The addition of 0.25 to 0.5 molar equivalents of 4-(dimethylamino)pyridine to a solution containing 25 results in a coalescence of the two anodic waves into a broad wave at +0.160 V, with the cathodic response at -0.17 V. Continued addition of 4-(dimethylamino)pyridine to 10 equivalents results in a sharpening of the anodic wave, with the cathodic response separating into two waves and shifting to more negative potentials. This behavior indicates a change from a quasi-reversible to an irreversible electron-transfer as the amount of 4-(dimethylamino)pyridine is increased. At ten equivalents, the anodic wave occurs at +0.178 V with the cathodic responses at -0.587 and -0.840 V (Figure 50D). At a scan rate of 1 V/s, the anodic wave consists of two overlapping waves; however, as the amount of 4-(dimethylamino)pyridine increases, there is less tendency for the anodic wave to separate. This electrochemical behavior is a result of the strong basicity of 4(dimethylamino)-pyridine. As 4-(dimethylamino)pyridine is added, the cyclic voltammogram indicates an irreversible process with the removal of the second electron occurring simultaneously with that of the first electron. This behavior more closely resembles that of dinuclear Rh(I) compounds in the presence of anionic-coordinating species than the previously investigated neutral-coordinating species.

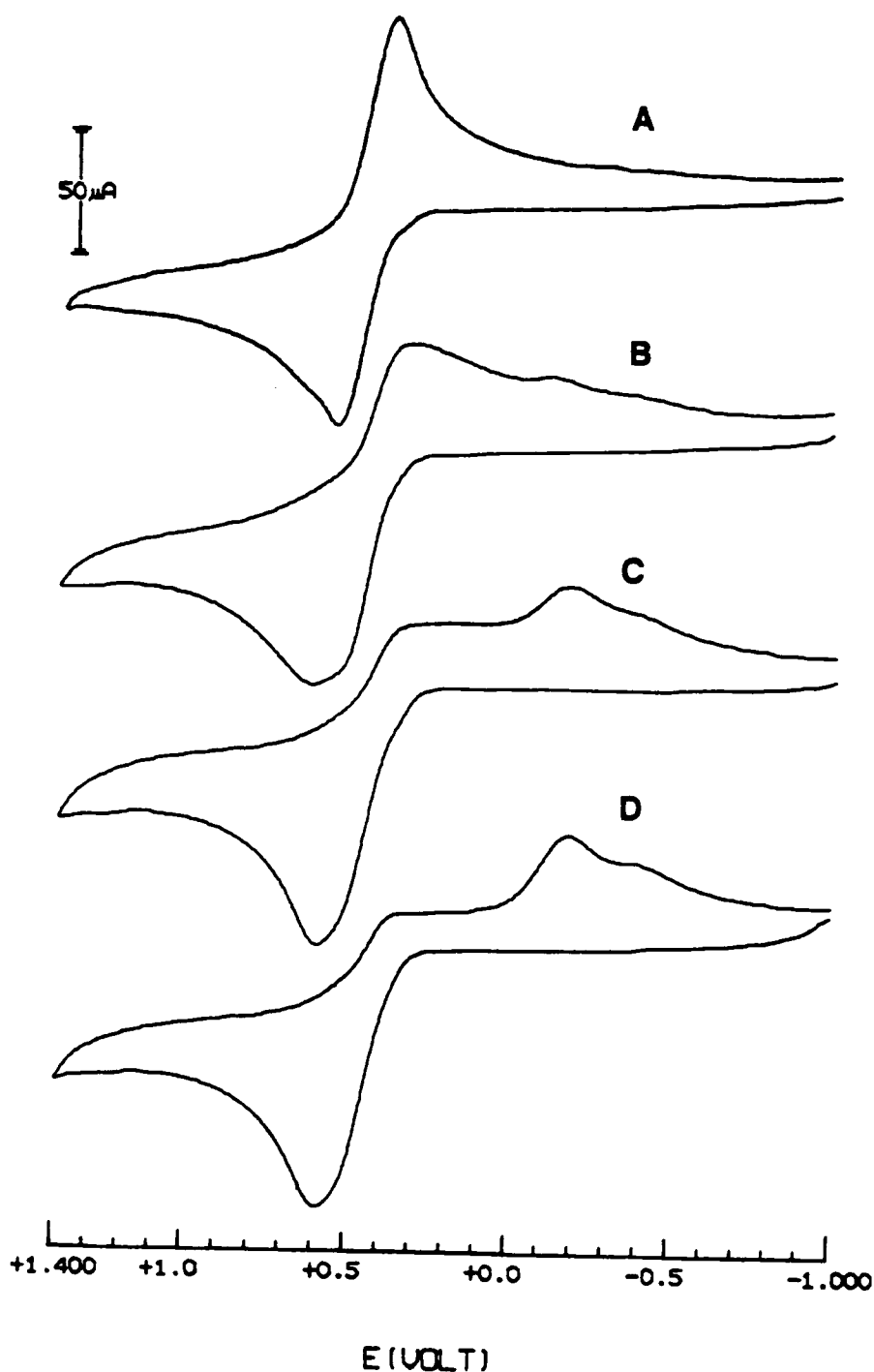


Figure 50. Cyclic voltammograms of 10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)_2$, 25, in a CH_2Cl_2 solution containing 0.1 M TBAH and (A) 0.25, (B) 3.0, (C) 5.0, and (D) 10.0 equivalents of 4-(dimethylamino)pyridine.

The cyclic voltammetric behavior of 25 in the presence of various pyridines is dependent on the basicity of the pyridine. The basicity of the pyridines used in this investigation increases in the order: pyridine < 3,5-dimethylpyridine < 4-(dimethylamino)pyridine with pK_b values 8.77, 7.66 and 4.29, respectively.¹⁰⁴⁻¹⁰⁶ The increase in basicity is based on the ability of the substituents to donate electron density into the pyridine ring. As the basicity increases, the strength of coordination between the pyridine moiety and the metal centers increases; thus, the ease with which the second electron is removed correlates with the basicity of the pyridine.

In summary, a comparison of the cyclic voltammograms of 25 in the presence of 20 equivalents of the various pyridines is shown in Figure 51. In the presence of pyridine, the result is a shift of the second anodic wave by 0.56 V, while the first one-electron couple remains essentially unchanged. This demonstrates that pyridine is interacting with the dinuclear Rh(1.5) center. Changing to a more basic pyridine, 3,5-dimethylpyridine, a shift of 0.75 V occurs for the second anodic wave. The increased basicity of 3,5-dimethylpyridine versus pyridine is demonstrated by a larger shift of the second oxidation wave as observed in the cyclic voltammogram of 25. In the presence of 20 equivalents of 4-(dimethylamino)pyridine, the cyclic voltammogram reveals an irreversible process with an anodic wave at +0.178 V with two corresponding cathodic waves at -0.55 and -0.79 V. The high basicity of 4-(dimethylamino)pyridine results in the increased interaction between the pyridine moiety and

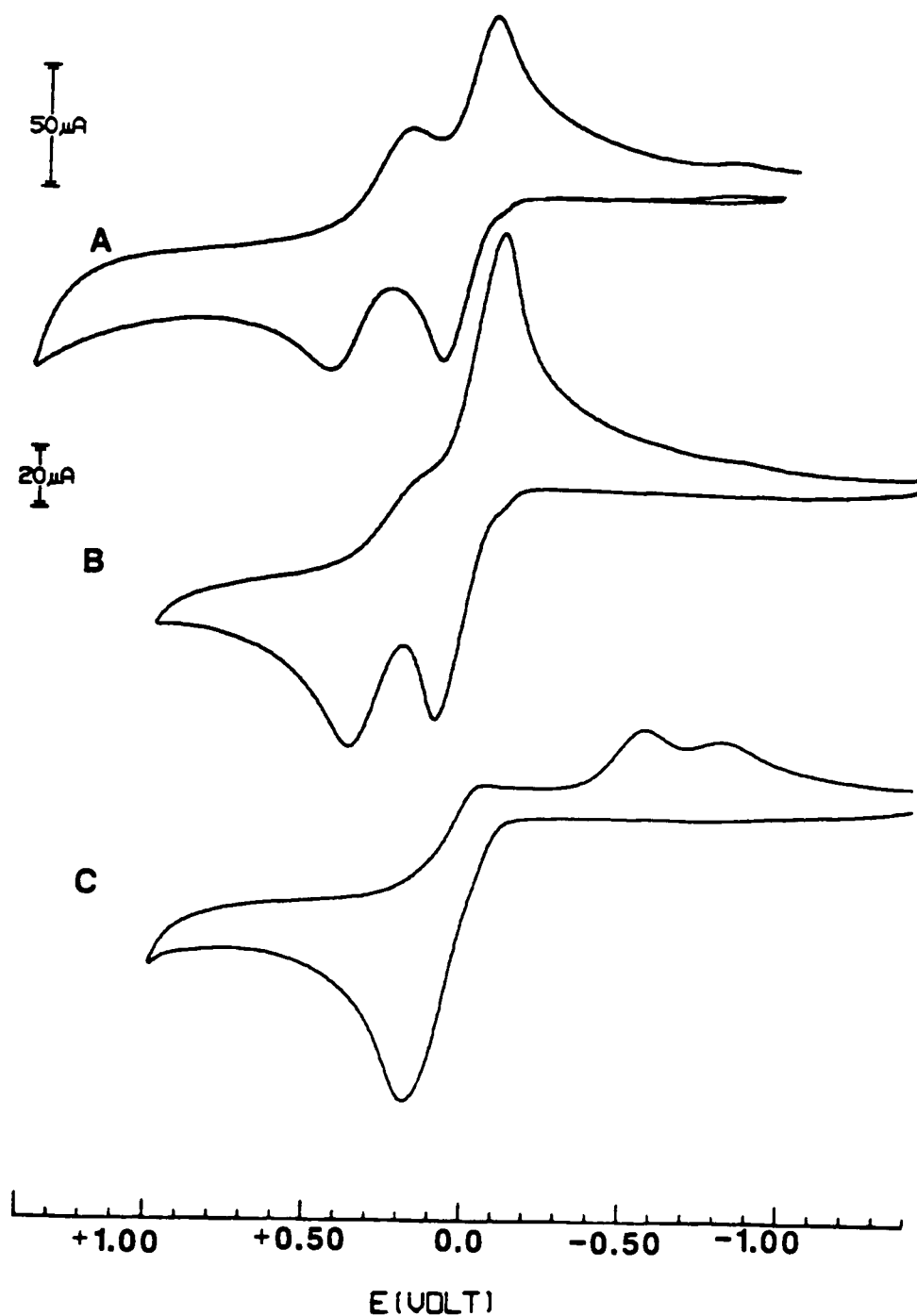


Figure 51. Cyclic voltammograms of 10^{-4} M $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-4MPz})](\text{PF}_6)$, 25, in a CH_2Cl_2 solution containing 0.1 M TBAH and 20 equivalents of (A) pyridine, (B) 3,5-dimethylpyridine, and (C) 4-(dimethylamino)pyridine.

the dinuclear Rh(I) complex. This strong interaction perturbs the electronic structure of the dinuclear unit such that an irreversible electrochemical process occurs.

G. Reactions of Dirhodium(I) Pyrazolate Complexes with Certain Acids

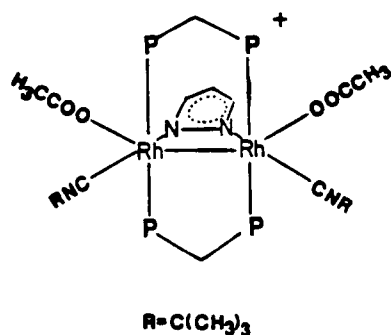
The ease with which 24-29 are oxidized and the propensity of H^+ to be reduced led to the study of the reactions of certain acids with 24-29. The acids were chosen based on the coordinating ability of the anions. The acids ranged from HCl, which contains a strong coordinating anion, Cl^- , to $HClO_4$, which contains a poor coordinating anion, ClO_4^- .

Addition of two equivalents of HCl to a methanol solution containing 25 results in a color change from purple-red to orange. The $^{31}P(H)$ NMR spectrum of the isolated product exhibits the typical symmetrical pattern observed for trans dppm-bridged dirhodium complexes with a chemical shift and $[^1J_{(Rh-P)} + ^xJ_{(Rh-P)}]$ value of 4.2 ppm and 90.3 Hz, respectively. The IR spectrum indicates the presence of terminal isocyanide ligands with CN bands at 2176(s) and 2170(sh) cm^{-1} , and also reveals PF_6^- bands at 839(s) and 557(m) cm^{-1} . The spectroscopic data obtained for the product obtained by treating 25 with HCl are identical to that obtained for $[Rh_2(\mu-dppm)_2(\underline{t}\text{-BuNC})Cl_2(\mu\text{-4MPz})](PF_6)$, 41. This result led to the investigation of other acids with weaker coordinating anions.

The addition of excess acetic acid to a THF solution of 24 results in a slight color change of the solution. Removal of the solvent from this solution results in a further color change of the

residue to yellow-orange. A yellow-gold solid is isolated from a CH_2Cl_2 solution of the resulting residue. The $^{31}\text{P}(\text{H})$ NMR spectrum of the isolated product exhibits a symmetrical AA'A''A'''XX' pattern with a chemical shift and $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 18.4 ppm and 95.2 Hz, respectively. The IR spectrum reveals a CN band at $2172(\text{s}) \text{ cm}^{-1}$ and PF_6^- bands at $839(\text{s})$ and $557(\text{m}) \text{ cm}^{-1}$. The IR spectrum also indicates the presence of terminal unidentate acetate ligands with C=O bands at $1601(\text{m})$ and $1574(\text{wsh}) \text{ cm}^{-1}$, and C-O bands at $1358(\text{m})$ and $1314(\text{m}) \text{ cm}^{-1}$. In unidentate acetate complexes, $\nu(\text{C=O})$ is higher and $\nu(\text{C-O})$ is lower than the respective frequencies observed in the free ion which have values at 1560 and 1416 cm^{-1} , respectively.⁹⁷

The NMR, IR and elemental analysis data are consistent with the formulation of the product obtained from 24 and acetic acid as $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{O}_2\text{CCH}_3)_2(\mu\text{-Pz})](\text{PF}_6)$, 71. The proposed structure of 71 is shown by VII.



VII

An identical product is obtained when methanol is employed as the solvent or by treating solid 24 with glacial acetic acid. The

$^{31}\text{P(H)}$ NMR data obtained for 71 is identical to the $^{31}\text{P(H)}$ NMR data obtained from the electrochemical oxidation of 24 in TBAB/TBAAC/acetone and the Rh(II) dimer generated in the acetate-induced disproportionation of 34 in acetone.

Reactions similar to those described above are observed for 25-29 in THF and 25 in methanol when treated with acetic acid generating 72-76, respectively. The $^{31}\text{P(H)}$ NMR and IR data for 71-76 are given in Table XX.

The cyclic voltammogram of 25 in a methanol solution containing 0.1 M TBAH reveals a quasi-reversible wave with an $E_{1/2}$ value at -0.025 V. The addition of excess acetic acid results in a green solution. The cyclic voltammogram reveals the absence of the anodic wave when the potential is cycled in the positive direction from +0.050 V. Exhaustive controlled-potential electrolysis at -0.100 V results in a color change from green to red with the reappearance of the anodic wave when the sweep is initiated as before. This procedure was repeated three consecutive times before the system deteriorated.

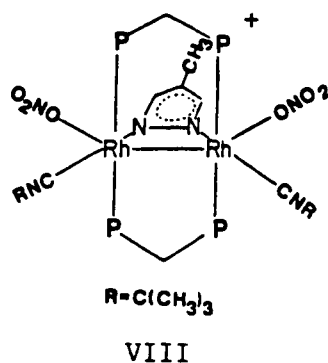
The addition of two equivalents of HNO_3 to a THF solution containing 25 results in a color change from red to orange, and the isolation of an orange solid. The $^{31}\text{P(H)}$ NMR spectrum of the isolated product exhibits a symmetrical AA'A''A'''XX' pattern, with a $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 92.8 Hz, indicative of a Rh dimer containing a metal-metal bond. The IR spectrum indicates the presence of terminal isocyanide ligands with a CN band at 2180(s) cm^{-1} and PF_6^- bands at 839(s) and 557(m) cm^{-1} . The IR spectrum also

TABLE XX

$^{31}\text{P(H)}$ NMR AND IR DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{OAc})_2(\mu\text{-Z})](\text{PF}_6)$

Z	$^{31}\text{P(H)}$ NMR			IR, cm^{-1}	
	δ , ppm	coupling constant ^a	νCN	$\nu\text{C=O}$	νCO
Pz, <u>71</u>	18.3	95.2	2172(s)	1601(m) 1574(wsh)	1358(m) 1314(m)
4MPz, <u>72</u>	18.45	95.2	2168(s)	1599(m) 1574(wsh)	1358(m) 1314(m)
345MPz, <u>73</u>	16.2	95.2	2168(s)	1609(m) 1599(m)	1358(m) 1314(m)
4B35MPz, <u>74</u>	16.1	95.2	2170(s)	1603(m)	1358(m) 1314(m)
345BPz, <u>75</u>	15.9	92.8			
Tz, <u>76</u>	17.2	95.2	2176(s)	1601(m) 1574(wsh)	1358(m) 1312(m)
^a $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, Hz					

contains bands at 1446(w), 1258(s), 1000(w) and 991(w) cm^{-1} due to coordinated nitrate ions.^{97,101} The bands assigned to nitrate are in the general region expected for coordinated nitrate ions. Although the stretching frequencies observed for coordinated nitrate are not conclusive in determining the mode of coordination, elemental analysis combined with NMR data are consistent with two unidentate nitrate ligands. The formulation of the product obtained from 25 and nitric acid is $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{NO}_3)_2(\mu\text{-4MPz})] \cdot (\text{PF}_6)$, 78, whose proposed structure is shown by VIII.



This structure give a coordination number of six, and an electron count of 18 for each Rh(II) atoms which supports the unidentate mode of coordination for the nitrate ligands. Similar products are obtained when 24, 26, 28 and 29 are treated with nitric acid in THF, thus generating 77 and 79-81, respectively. The $^{31}\text{P}(\text{H})$ NMR and IR data for 77-81 are given in Table XXI. The $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$ value obtained for the dinuclear Rh(II) complex generated by the electrochemical oxidation of 28 in TBAN/ CH_2Cl_2 is identical to that

TABLE XXI

$^{31}\text{P}\{\text{H}\}$ NMR AND IR DATA FOR COMPLEXES OF THE TYPE
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\text{NO}_3)_2(\mu\text{-Z})](\text{PF}_6)$

Z	$^{31}\text{P}\{\text{H}\}$ NMR			IR, cm^{-1}		
	δ , ppm	coupling constant ^a	νCN	νNO_2	νNO_2	$\nu\text{N=O}$
Pz, <u>77</u>	16.2	92.8	2182(s)	1466(w)	1258(s)	1003(w) 1002(w)
4MPz, <u>78</u>	16.2	92.8	2180(s)	1466(w)	1258(s)	1000(w) 991(w)
35MPz, <u>79</u>	14.3	92.8	2178(s)	1462(w)	1258(s)	1001(w) 1011(w)
4B35MPz, <u>80</u>	14.2	92.8	2180(s)	1462(w)	1258(s)	1001(w)
345BPz, <u>81</u>	14.2	92.8	2182(s)	1464(w)	1256(s)	991(w)
^a $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, Hz						

of 80. However, the chemical shift is shifted downfield by 0.85 ppm which could be a result of TBAN present in the NMR sample. The product obtained from 27 and nitric acid results in a broad phosphorus resonance in the $^{31}\text{P}(\text{H})$ NMR spectrum, and has defied characterization.

The reactions of 24-26, 28 and 29 with H_2SO_4 in THF generates the dinuclear $\text{Rh}(1.5)$ complexes, 34-38, respectively. The reaction of 27 and H_2SO_4 in THF results in a decomposition of 27 as determined by the $^{31}\text{P}(\text{H})$ NMR spectrum. However, the reaction of 26 and H_2SO_4 or HNO_3 in methanol generates a green solid. The NMR spectrum of the isolated product reveals an AA'A''A'''XX' pattern with a chemical shift and $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$ value of 28.3 ppm and 117.2 Hz, respectively. The IR spectrum indicates the presence of terminal isocyanide ligands with a CN band at $2168(\text{s}) \text{ cm}^{-1}$, and the presence of PF_6^- with bands at $839(\text{s})$ and $557(\text{m}) \text{ cm}^{-1}$. After observing a thermochromic effect for this product similar to that observed for the dinuclear $\text{Rh}(1.5)$ compounds, an ESR spectrum was obtained to determine if this product was paramagnetic. The room-temperature CH_2Cl_2 solution ESR spectrum reveals an anisotropic pattern (Figure 52), with observable components at $g = 2.02$, 2.16 and 2.22 . Although this product is paramagnetic, it is not identical to 36, which shows an isotropic room-temperature CH_2Cl_2 solution ESR pattern with a g value of 2.15 . The g values at 2.02 , 2.16 and 2.22 are in the range observed for 34-37 at 77 K . The reason for the observed anisotropic pattern at room-temperature and the reason why a $^{31}\text{P}(\text{H})$ NMR spectrum can be obtained are unclear.

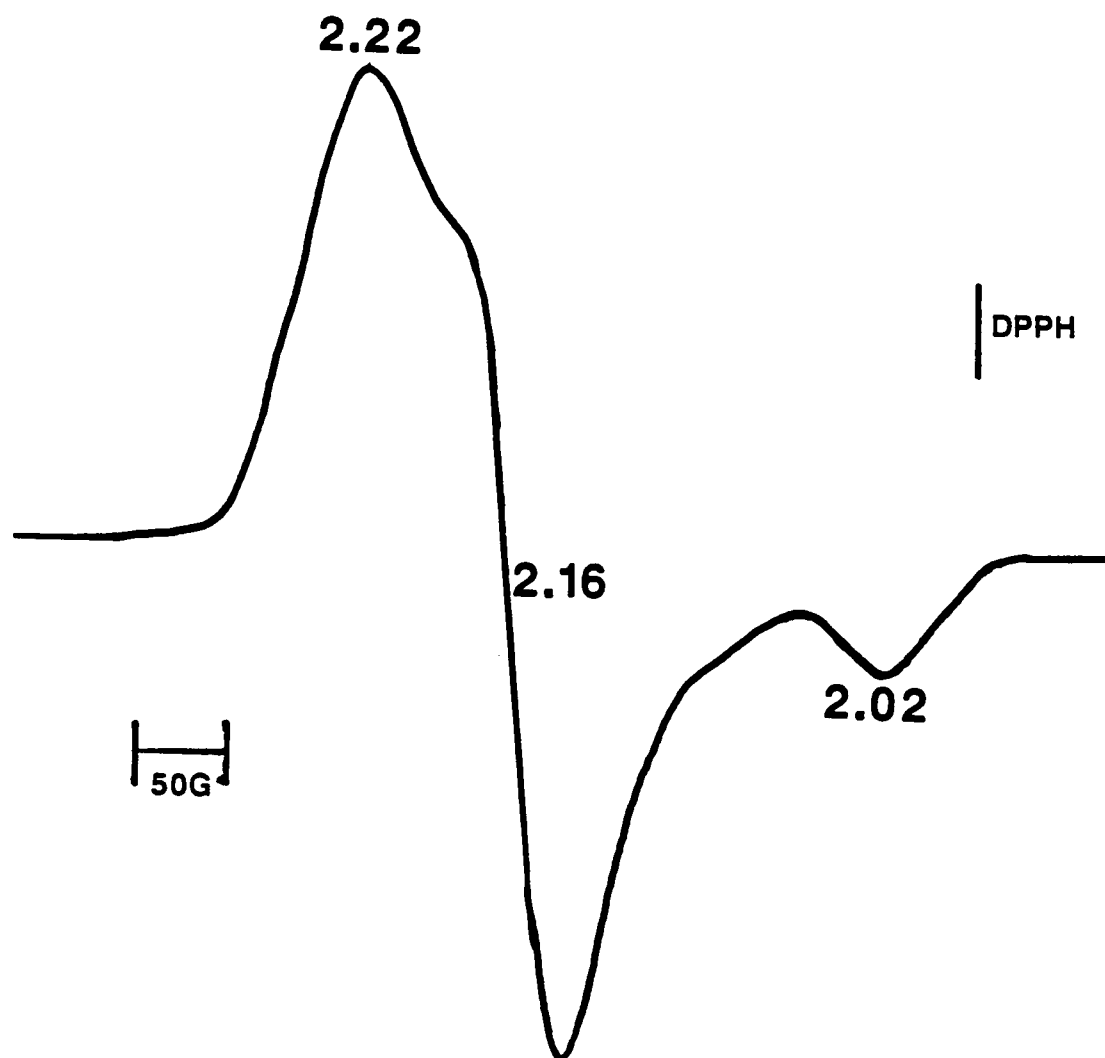


Figure 52. Room-temperature ESR spectrum of the product obtained from the reaction of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)$, 26, with H_2SO_4 in methanol.

Slow diffusion of ether/hexanes into a CH_2Cl_2 solution containing the product from the reaction of 26 and H_2SO_4 in methanol generated dark-purple prismatic crystals. The room-temperature solution ESR spectrum of these crystals is identical to that of 36.

Given in Appendix B are: (1) Experimental details, (2) Intensity measurements, (3) Structure solutions and refinement, (4) Positional parameters and their estimated standard deviations, (5) Bond distances, and (6) Bond angles. Anisotropic thermal parameters and calculated and observed structural factors are available.¹⁰²

The crystal structure of 36 consists of a cationic dinuclear $\text{Rh}(1.5)$ species and hexafluorophosphate anions in a 1:2 ratio. The structure of the dinuclear species with atomic numbering is shown in Figure 53. Complex 36 contains two $\text{Rh}(1.5)$ metal atoms held together by one 35MPz and two dppm bridging ligands. The geometry about each rhodium atom is square pyramidal, with one rhodium atom in the center of the square plane, and the other rhodium atom forming the apex of the pyramid. Each rhodium atom is coordinated to two trans-phosphorus atoms of the dppm bridging ligand, a nitrogen atom of the bridging 35MPz ligand, a carbon atom from the t-butylisocyanide, and the other rhodium atom by a bond of order 0.5.

The 0.5 bond order is reflected in the Rh-Rh bond distance of 2.83 Å. This bond distance is longer than the Rh-Rh single bond lengths of 40 (2.768 Å) and $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2\text{I}_2(\mu\text{-35MPz})]^+$ (2.725 Å),³¹ and shorter than that of 19 (3.060 Å).³¹ However, the Rh-Rh bond distance of 2.83 Å observed for 36 is in the upper range

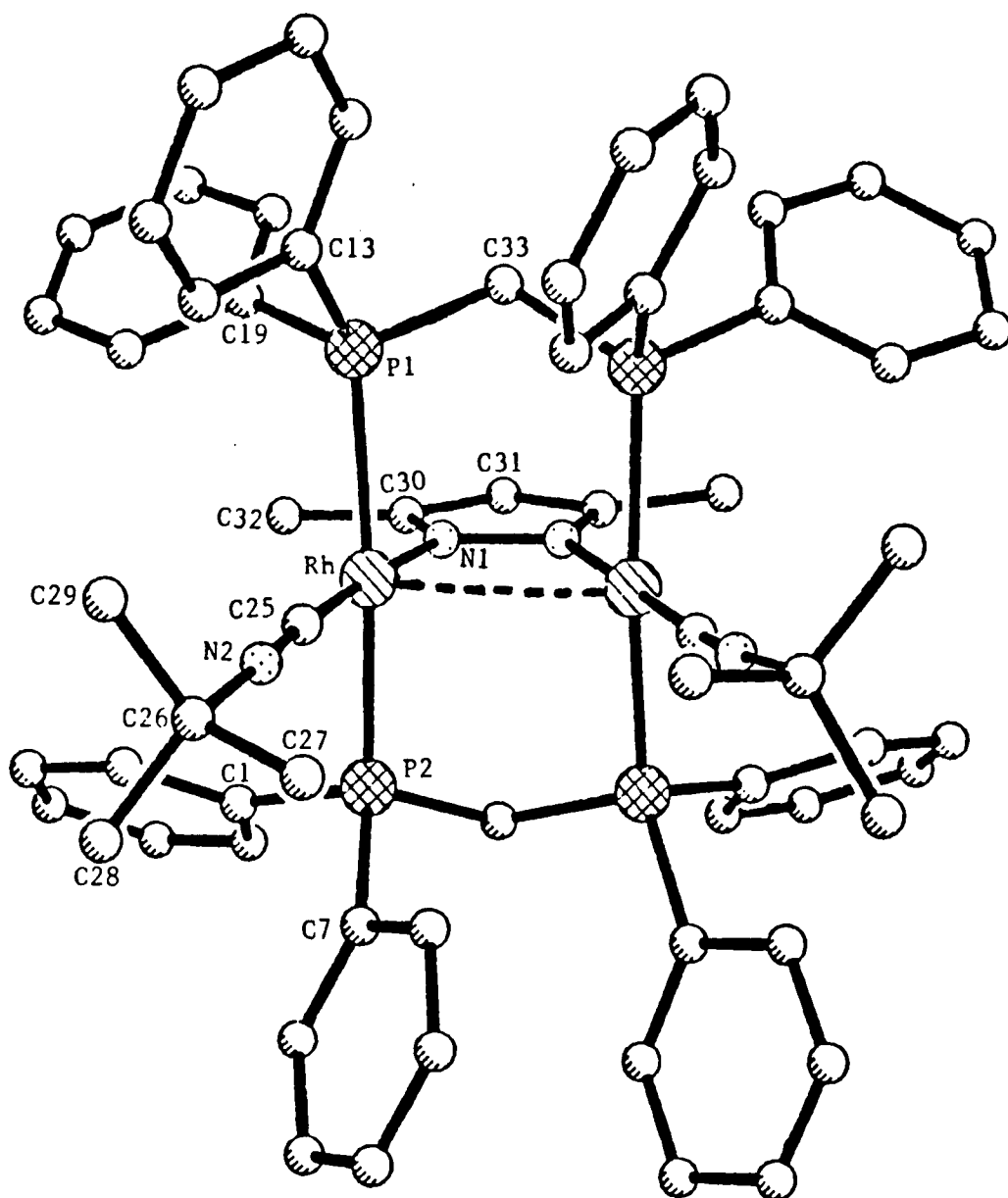


Figure 53. Structure of $[\text{Rh}_2(\mu\text{-dppm})_2(\eta\text{-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$, **36**. The hydrogen atoms are omitted for clarity, and the carbon atoms in the phenyl rings are sequentially numbered around the ring.

observed for binuclear A-frame complexes containing a single metal-metal bond.²⁸ This value signifies considerable Rh-Rh interaction for 36.

The Rh-C ($\underline{t}$ -BuNC) and Rh-N (pyrazolate) bond distances of 1.928 and 2.071 Å, respectively, are within experimental error of the respective bond lengths observed for complex 40, a dinuclear Rh(II) complex. Other significant bond lengths are the Rh-P1 and Rh-P2 (dppm) distances of 2.300 and 2.351 Å, respectively, which are similar to 18, a dinuclear Rh(I) complex.

The bond angles that comprise the square-pyramidal geometry about each rhodium atom are: P1-Rh-P2, 167.2°; P1-Rh-N1, 85.5°; P1-Rh-C25, 92.4°, P2-Rh-N1, 84.6°, P2-Rh-C25, 98.0°; and N1-Rh-C25, 176.3°.

Unlike 40, the methylene groups of the dppm ligands are folded over the bridging pyrazolate ligand, which is the orientation observed for most trans dppm-bridged dinuclear rhodium A-frames.^{13-15,25,27-31}

Acid reactions involving the weakest coordinating anion were then investigated. The reaction of 26 and HClO₄ in a THF solution results in the isolation of a green solid after recrystallization from CH₂Cl₂. The IR spectrum reveals CN bands at 2168(s) and 2157(sh) cm⁻¹, and PF₆⁻ bands at 839(s) and 557(m) cm⁻¹. The IR spectrum also reveals the presence of ClO₄⁻ with ClO₄⁻ bands at 1098(s), 1084(s) and 625(m) cm⁻¹. The ³¹P{H} NMR spectrum reveals a symmetrical AA'A''A'''XX' pattern with a chemical shift and [¹J_(Rh-P) + ^xJ_(Rh-P)] value of 27.97 ppm and 117.2 Hz, respectively.

Analogous reactions are observed for 24, 25, 28 and 29 with HClO_4 . The IR and $^{31}\text{P(H)}$ NMR data of the products obtained are given in Table XXII. The product obtained from the reaction of 28 with HClO_4 and the product obtained from the reaction of 29 and HClO_4 do not contain PF_6^- , only bands ascribed to ClO_4^- are present in the IR spectra. When the product is isolated from the initial reaction solution and is not recrystallized from CH_2Cl_2 , the $^{31}\text{P(H)}$ NMR spectrum reveals a pattern indicative of the phosphorus atoms being in different chemical environments. The $^{31}\text{P(H)}$ NMR spectrum shown in Figure 54 is that of 28, isolated in THF, and reveals a phosphorus resonance centered at 21.9 ppm, and the AA'A''A'''XX' pattern observed when the product is recrystallized from CH_2Cl_2 . Upon recrystallization, the product gives rise to the typical AA'A''A'''XX' pattern. The initial product could be a solvated adduct which loses the coordinated solvent upon recrystallization in CH_2Cl_2 and generates the complexes for which spectroscopic data have been obtained.

Elemental analysis indicates that a product obtained from the reaction of 28 and HClO_4 and recrystallized from CH_2Cl_2 is $[\text{Rh}_2(\mu\text{-dppm})_2(\mu\text{-BuNC})_2(\mu\text{-4B35MPz})(\text{ClO}_4)_2]$. Also, the spectroscopic and analytical data for the products obtained from the reaction of 26 with $\text{H}_2\text{SO}_4/\text{MeOH}/\text{PF}_6^-$ and that with $\text{HClO}_4/\text{THF}/\text{PF}_6^-$ are very similar, and both show a thermochromic effect upon freezing to 77 K. The only difference between the two products is the counter ions present. A coordinating ClO_4^- , as suggested by the IR data in Table XXII, could result from weak interaction between ClO_4^- and the

TABLE XXII

SPECTROSCOPIC DATA OBTAINED FROM THE PRODUCTS OF
THE REACTIONS OF $[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t-BuNC}})_2(\mu\text{-Z})](\text{PF}_6)$ AND HClO_4

Z	$^{31}\text{P(H)} \text{ NMR}$		IR, cm^{-1}	
	δ , ppm	coupling constant ^a	νCN	νClO_4^-
Pz, <u>24</u>	28.7	119.6	2174(s)	1098(s) 1085(sh) 623(m)
4MPz, <u>25</u>	28.3	119.6	2174(s)	1096(s) 1087(sh) 623(m)
35MPz, <u>26</u>	27.97	117.2	2168(s) 2157(sh)	1098(s) 1084(s) 625(m)
4B35MPz, <u>28</u>	27.6	117.2	2172(s)	1098(s) 1092(sh) 625(m)
345BPz, <u>29</u>	25.99	114.7	2176(s)	1096(s) 1086(sh) 625(m)
^a $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$, Hz				

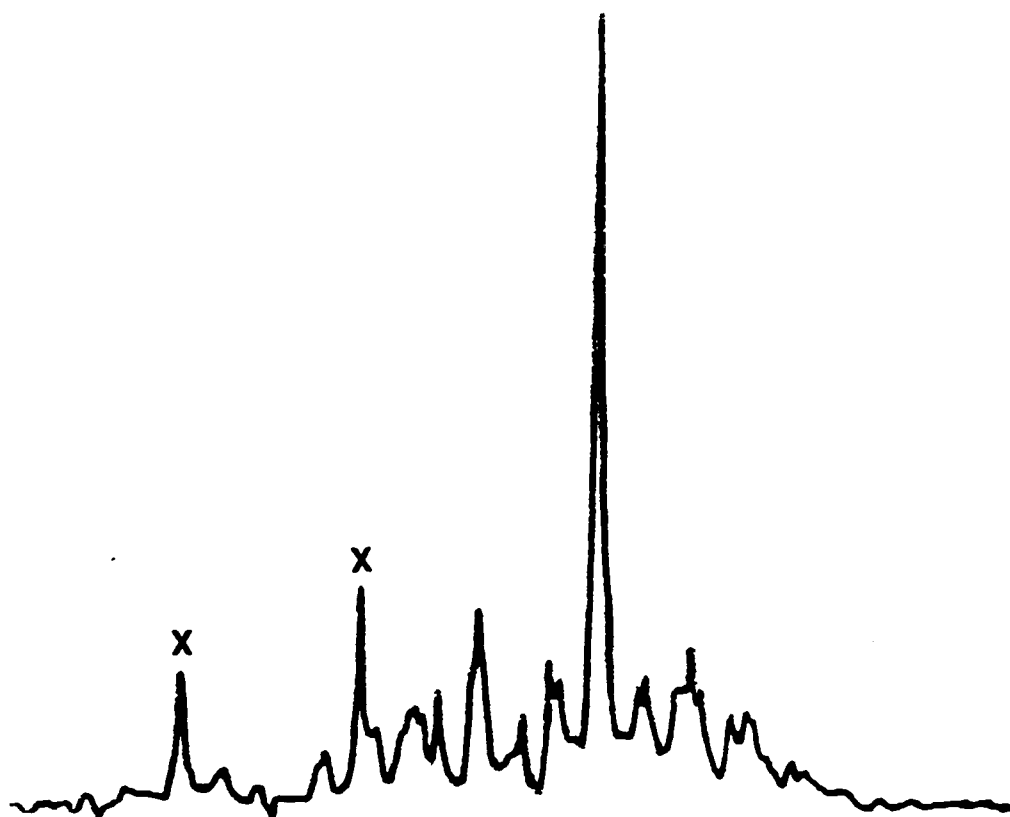


Figure 54. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of the product obtained from a THF solution containing 28/ $\text{HClO}_4/\text{PF}_6^-$; X denotes the major lines of the AA'A''A'''XX' pattern.

rhodium atoms. The two products that do not contain PF_6^- counter ions are those which contain anodic waves at the most positive potentials. This indicates that the rhodium atoms have a higher positive charge, and therefore result in an increased interaction between the rhodium complex and ClO_4^- .

The obtainment of paramagnetic or dinuclear $\text{Rh}(1.5)$ complexes from the reactions of 24-27, 28 and 29 with HClO_4 is further exemplified by a disproportionation reaction. The addition of one equivalent acetate to the $\text{25/HClO}_4/\text{PF}_6^-$ product results in the formation of 25 and 72 as determined by NMR spectroscopy. It is unclear why $^{31}\text{P}(\text{H})$ and ^1H NMR spectra show no indication of line broadening imposed by the unpaired electron for the $\text{Rh}_2/\text{HClO}_4$ products and the product obtained from the reaction of 26 with H_2SO_4 in methanol. One possibility is that the unpaired electron is isolated from the nuclei being observed by NMR spectroscopy, and does not affect its relaxation time. Another reason could be the electron is rapidly changing its spin state, and thus the oscillating magnetic field due to the unpaired electron will average out to zero. The electron now becomes less efficient at relaxing the nucleus being investigated by NMR spectroscopy.

CHAPTER VI

CHEMISTRY AND ELECTROCHEMISTRY OF TETRANUCLEAR RHODIUM COMPLEXES CONTAINING BIPYRAZOLATE BRIDGING LIGANDS WITH TERMINAL CARBONYL AND ISOCYANIDE LIGANDS

The interesting chemistry observed for the dinuclear pyrazolate complexes led to the investigation of tetranuclear rhodium complexes; that is, two $\text{Rh}_2(\mu\text{-dppm})_2\text{L}_2$ ($\text{L}=\text{CO}, \text{t-BuNC}$) fragments joined together by a bridging bipyrazolate ligand. The two bipyrazolate ligands employed are 4,4'-methylenebis(3,5-dimethylpyrazolate) and 3,3',5,5'-tetramethylbipyrazolate. The addition of the stoichiometric amounts of K_2mbPz or K_2bPz to 1 generates 58 and 57, respectively. In the midst of the investigation of 58 and 57, a paper by Oro et al.³¹ was published with the synthesis of 57.

The IR spectra of 57 and 58 indicate the presence of terminal carbonyl ligands with CO stretching frequencies between 1960 and 2010 cm^{-1} , and PF_6^- counter-ion bands at 839(s) and 557(m) cm^{-1} (Table XXIII). The $^{31}\text{P}(\text{H})$ NMR spectra of 57 and 58 reveal a symmetrical pattern similar to trans-dppm dinuclear rhodium complexes which exhibit a $\text{AA}'\text{A}''\text{A}''' \text{XX}'$ spin system. The chemical shifts of approximately 22.0 ppm and $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ values of 129 Hz exhibited by 57 and 58 (Table XXIII) are similar to those obtained for 18-23.

Addition of four equivalents of t-BuNC to 57 and 58 results in the displacement of the carbonyl ligands generating 59 and 60, respectively. The IR spectra of 59 and 60 indicate the presence of

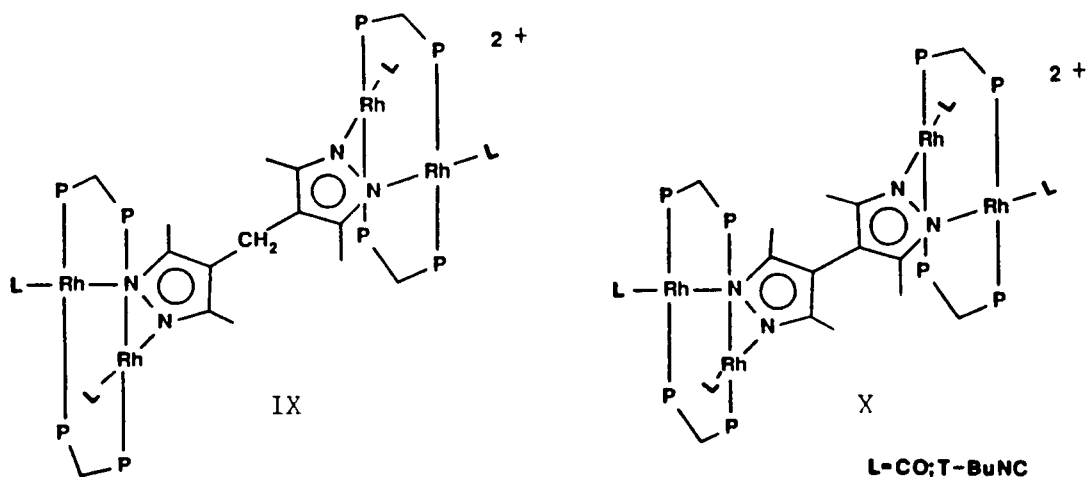
TABLE XXIII

$^{31}\text{P(H)}$ NMR AND IR DATA FOR COMPOUNDS OF THE TYPE
 $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{L})_2]_2(\mu\text{-Z})\}(\text{PF}_6)_2$

L	Z	<u>IR</u>		<u>NMR</u>	
		$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CN}), \text{cm}^{-1}$	δ, ppm	coupling constant, Hz
CO	bPz, <u>57</u>	1985(s) 1971(m)		22.3	129.4
CO	mbPz, <u>58</u>	1962(s) 1971(m) 1990(m) 2006(m)		22.2	129.4
<u>t</u> -BuNC	bPz, <u>59</u>		2100(s) 2072(m)	19.5	141.6
<u>t</u> -BuNC	mPz, <u>60</u>		2110(s) 2075(sh)	19.7	139.2

terminal isocyanide ligands with CN bands between 2070 and 2115 cm^{-1} , and PF_6^- counter-ion bands at 839(s) and 557(m) cm^{-1} (Table XXIII). The $^{31}\text{P}\{\text{H}\}$ NMR spectra of 59 and 60 reveal a symmetrical pattern similar to the NMR pattern observed for 57 and 58 with $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ values of approximately 140 Hz (Table XXIII).

The major difference between the mbPz and bPz complexes is the insertion of a methylene group separating the two pyrazolate groups in 58 and 60. The methylene group between the pyrazolate moieties interrupts the delocalized Π system between the pyrazolate groups, and thus between the two $\text{Rh}_2(\mu\text{-dppm})_2\text{L}_2$ ($\text{L}=\text{CO}, \underline{\text{t}}\text{-BuNC}$) units. This difference is the basis for the comparison of the chemical and electrochemical behavior between the mbPz and bPz complexes. Possible structures for these complexes are shown by IX and X.



The correct orientation of the dinuclear $\text{Rh}(\text{I})$ fragments in the mbPz structure can only be ascertained by structural analysis.

The replacement of the carbonyl ligands with isocyanide results in the low-energy UV-Vis electronic transition shifting to lower energy (Table XXIV). This trend correlates with the behavior observed for the dinuclear rhodium pyrazolate complexes as CO is replaced with *t*-BuNC. The same MO description that was proposed for the dinuclear rhodium complexes applies to the tetranuclear rhodium complexes since they are composed of two dinuclear units and a pyrazolate ligand at the bridgehead position. However, in the dinuclear fragment, the pyrazolate ligand contains a larger substituent in the four position. The stronger interaction between the carbonyl π^* and Rh $d \pi$ orbitals results in a lowering of the HOMO compared to the isocyanide ligand (Figure 19, page 145), and thus the low-energy transition occurs at higher energy for the carbonyl compounds.

The cyclic voltammogram of 57 in a CH_2Cl_2 solution containing 0.1 M TBAH exhibits irreversible oxidation waves at +0.54 and +0.797 V, with the cathodic responses at +0.490, -0.305 and -0.528 V (Figure 55A). Cycling the potential in an increasingly negative direction reveals two overlapping cathodic waves at -1.8 and -1.92 V with no observable anodic responses. If the potential is cycled twice through the anodic and corresponding cathodic waves without cleaning the working electrode, the cathodic waves at +0.490 and -0.528 V disappear, and the major cathodic wave shifts to -0.44 V during the second cycle (Figure 55B). Controlled-potential

TABLE XXIV

LOWEST ENERGY UV-VIS TRANSITION FOR
 $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{L})_2]_2(\mu\text{-Z})\}(\text{PF}_6)_2$ COMPLEXES

Z	<u>λ_{max}, nm</u>	
	L-CO	L-t-BuNC
bPz	492	509
mbPz	491	511

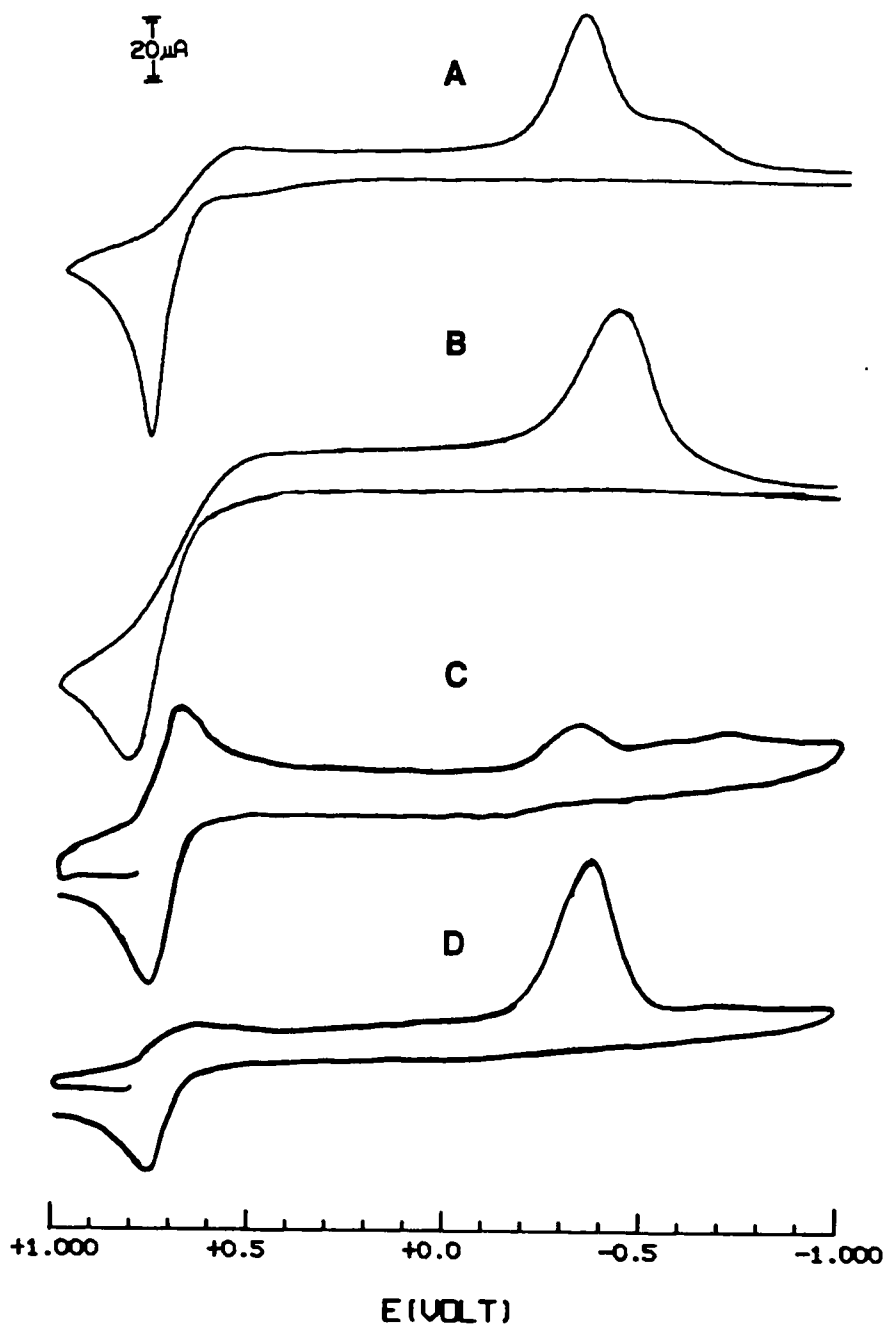


Figure 55. Cyclic voltammograms of 10^{-3} M $([\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2]_2(\mu\text{-bPz}))(\text{PF}_6)_2$, 57 in CH_2Cl_2 and 0.1 M TBAH (A) first potential cycle before bulk oxidation, (B) second potential cycle before bulk oxidation, (C) first potential cycle after bulk oxidation, and (D) second potential cycle after bulk oxidation.

coulometry at +0.850 V indicates that 57 undergoes a two-electron oxidation. During bulk electrolysis, the working electrode had to be cleaned repeatedly due to coating of the oxidized product. The cyclic voltammogram of the brown-green oxidized solution reveals two cathodic waves at +0.694 and -0.320 V, and an anodic wave at +0.764 V (Figure 55C). If the electrode is not polished and the potential cycled again, the cathodic wave at +0.694 V decreases, and the cathodic wave at -0.40 V increases (Figure 55D)

The reduction wave at +0.694 V could result from the oxidized product in solution, and the reduction wave at -0.320 V in response to the adsorbed-oxidized product. This behavior is consistent with the cyclic voltammetric behavior of 57 in TBAH/CH₂Cl₂ when the scan rate is increased to 50 V/s. The cyclic voltammogram of 57 at a scan rate of 50 V/s exhibits a cathodic wave at +0.4 V. This wave appears at fast scan rates since adsorption of the oxidized species on the electrode surface is at a minimum.

The cyclic voltammetric behavior of 57, after the potential is stepped to +0.90 V and held until the current decreases, indicates that the oxidized species has been absorbed on the electrode surface. When the potential is initiated from 0.0 V, the cyclic voltammogram reveals an anodic wave at +0.734 V in the initial sweep segment, and a cathodic wave at -0.575 V in the second segment (Figure 56A). Cycling the potential again without polishing the electrode results in an increase in the anodic wave and a decrease in the cathodic response (Figure 56A). The i_{pc}/i_{pa} ratio of 5.0 and the distortion of the cathodic wave from the symmetrical parabolic

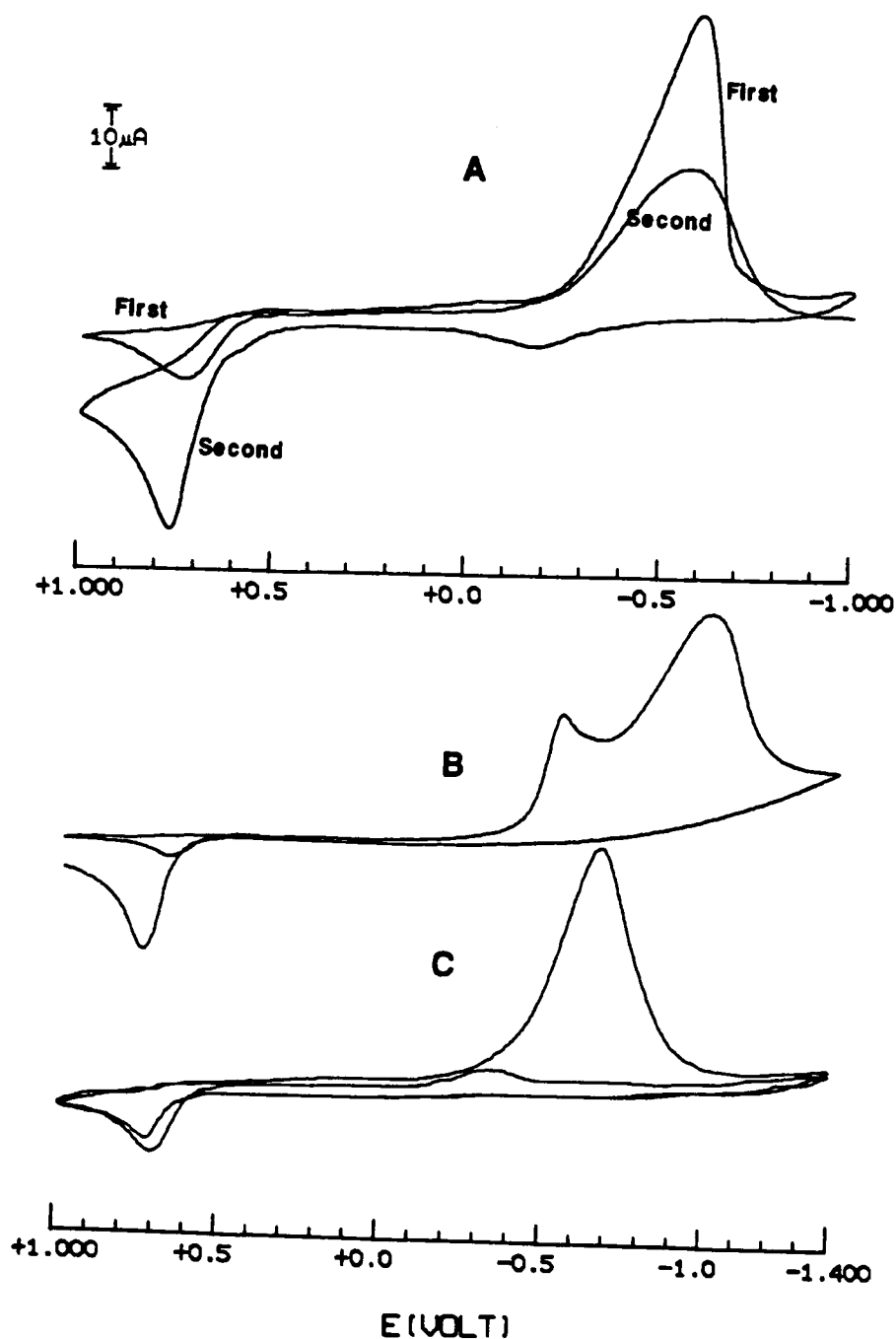


Figure 56. Cyclic voltammograms of 10^{-3} M $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2]_2(\mu\text{-bPz})\}(\text{PF}_6)_2$, 57, in CH_2Cl_2 and 0.1 M TBAH after stepping the potential to +0.90 V (A) first and second potential cycle in the same electrolyte solution (B) first potential cycle after transferring the rinsed working electrode to a neat electrolyte solution, and (C) second potential cycle in the neat electrolyte solution.

shape, shown in the cyclic voltammogram of the initial cycle, indicates adsorption of the oxidized species on the working electrode (Figure 56A).⁹² When the potential is stepped to +0.90 V and the rinsed electrode is transferred to a neat electrolyte solution, an anodic wave at +0.676 V and two cathodic responses at -0.53 and -0.98 V are noted (Figure 56B). An additional potential cycle reveals a single anodic and cathodic wave at +0.72 and -0.70 V, respectively (Figure 56C). The observation of electroactive behavior in the neat electrolyte solution confirms adsorption of the oxidized product of 57 on the electrode surface.

The presence of an anodic wave in the initial sweep segment indicates unoxidized 57 in the adsorbed layer. Although the oxidized species is semi-insoluble in CH_2Cl_2 , a pure product could not be obtained. An IR spectrum of the oxidized species was acquired by IR spectroelectrochemistry. The IR spectrum of 57 in a CH_2Cl_2 solution containing 0.1 M TBAH at a rest potential of 0.0 V reveals two CO bands at 1995(s) and 1981(m) cm^{-1} . The IR spectrum after stepping the potential to +0.95 V indicates terminal CO ligands with CO stretching frequencies at 2060(s) and 2033(w) cm^{-1} . Stepping the potential to -0.8 V indicates that 57 has been regenerated. The IR spectrum reveals the reappearance of CO bands at 1995(s) and 1981(m) cm^{-1} . In addition to the electrochemical data, the increase of approximately 60 cm^{-1} in the CO stretching frequencies and the absence of CO bands in the region usually observed for CO bound to Rh(I) indicates that each dinuclear unit has undergone a one-electron oxidation. An increase of

approximately 60 cm^{-1} has also been observed for a one-electron oxidation of 18-20, 22 and 23. Based on the IR and electrochemical data, the oxidized compound that adsorbs on the electrode surface is presumably $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2]_2(\mu\text{-bPz})\}(\text{PF}_6)_4$.

The cyclic voltammogram of 58 in a CH_2Cl_2 solution containing 0.1 M TBAH exhibits an anodic wave at +0.80 V and cathodic waves at +0.679 and -0.503 V (Figure 57). Sweeping the potential in an increasingly negative direction reveals two overlapping cathodic waves at -1.72 and -1.82 V with two corresponding anodic waves at -0.183 and +0.648 V. Controlled-potential coulometry at +1.0 V indicates that 58 undergoes a two-electron oxidation. Analysis of the cyclic voltammetric data for the two-electron couple is given in Table XXV and indicates: (1) the midpoint potentials, $E_{1/2}$, were invariant with sweep rate; (2) the values of ΔE , the potential difference between E_{pa} and E_{pc} , increase as the sweep rate increases; (3) the ratios of the peak current, $i_{\text{pc}}/i_{\text{pa}}$, decrease with increasing scan rate; and (4) the values for i_{pa} were proportional to the square root of the potential sweep rate. This behavior is indicative of a quasi-reversible couple⁸⁷⁻⁸⁹ except that the $i_{\text{pc}}/i_{\text{pa}}$ ratio shows variation with scan rate.

The differences in the cyclic voltammetric behavior of 57 and 58 are a consequence of the methylene group joining the two pyrazolate moieties in 58. The delocalization of the Π system between the two dimeric units has a profound effect on the electrochemical behavior of 57. The delocalization of the Π system plus the strong Π -acid carbonyl ligand results in adsorption and an irreversible

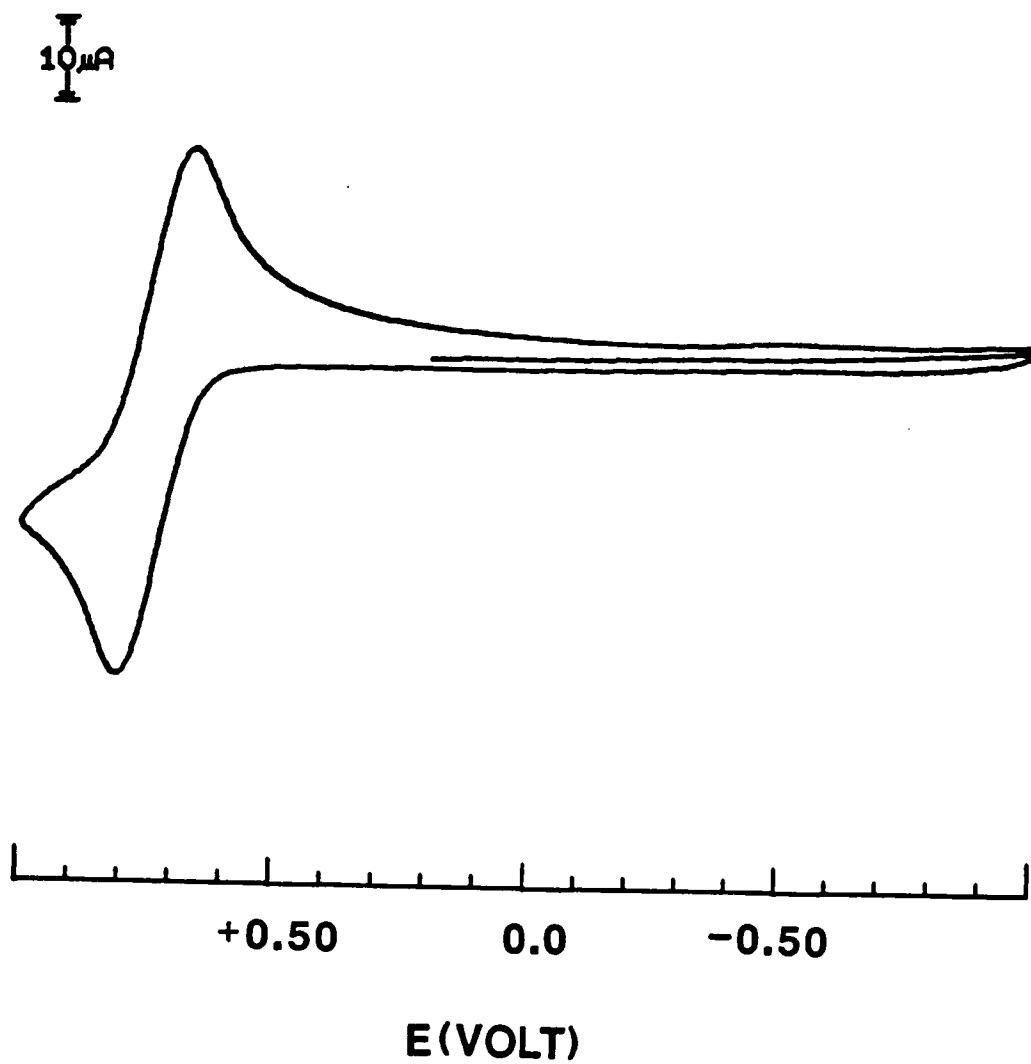


Figure 57. Cyclic voltammogram of 10^{-3} M $(\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2)_2(\mu\text{-mbPz})(\text{PF}_6)_2$, 58, in CH_2Cl_2 and 0.1 M TBAH.

TABLE XXV

CYCLIC VOLTAMMETRIC DATA FOR COMPOUND
 $([\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})_2]_2(\mu\text{-mbPz}))(\text{PF}_6)_2$

Compound #	v^a	E_{pa} , V	E_{pc} , V	ΔE , V	$E_{1/2}$, V	i_{pc}/i_{pa}
<u>58</u>	50	0.75	0.65	0.10	0.70	0.99
	100	0.75	0.65	0.10	0.70	0.98
	200	0.76	0.64	0.12	0.70	0.97
	300	0.77	0.63	0.14	0.70	0.96
	400	0.77	0.63	0.14	0.70	0.94
	500	0.79	0.63	0.16	0.71	0.89

^a Sweep rate in mV/s

electron-transfer reaction. In the case of 58, there is no delocalization of the π -system and as a result the electrochemical behavior is moderately similar to that obtained for 18-20, 22 and 23.

The addition of t-BuNC to 57 and 58 generating 59 and 60, respectively, has a direct effect on the cyclic voltammetric behavior of 59 and 60 compared to their tetracarbonyl counterparts. Whereas the cyclic voltammograms of 57 and 58 differ from 18-20, 22 and 23 in TBAH/ CH_2Cl_2 , the cyclic voltammograms of 59 and 60 resemble those of 24-29. Figure 58 illustrates a typical cyclic voltammogram observed for 59 and 60 in a CH_2Cl_2 solution containing 0.1 M TBAH. The cyclic voltammogram of 60 exhibits two anodic waves at +0.170 and +1.223 V, with the respective cathodic responses at +0.002 and +0.675 V (Figure 58). The similarities between the cyclic voltammograms of 59 and 60 with those of 24-29 are probably a consequence of the increased electron density on the rhodium atoms brought about by the weaker π -acid isocyanide ligands.

Controlled-potential coulometry past each anodic wave of 59 and 60 indicates that each oxidation wave corresponds to a two-electron process. Analysis of the cyclic voltammetric data for the first two-electron couple is given in Table XXVI and reveals:

- (1) the $E_{1/2}$ values were essentially invariant with scan rate;
- (2) the ΔE values increase as the sweep rate increases; (3) the i_{pc}/i_{pa} ratios were constant with scan rate; and (4) the values of i_{pa} were proportional to the square root of the potential sweep rate. This behavior is consistent with a quasi-reversible two-electron couple.⁸⁷⁻⁸⁹

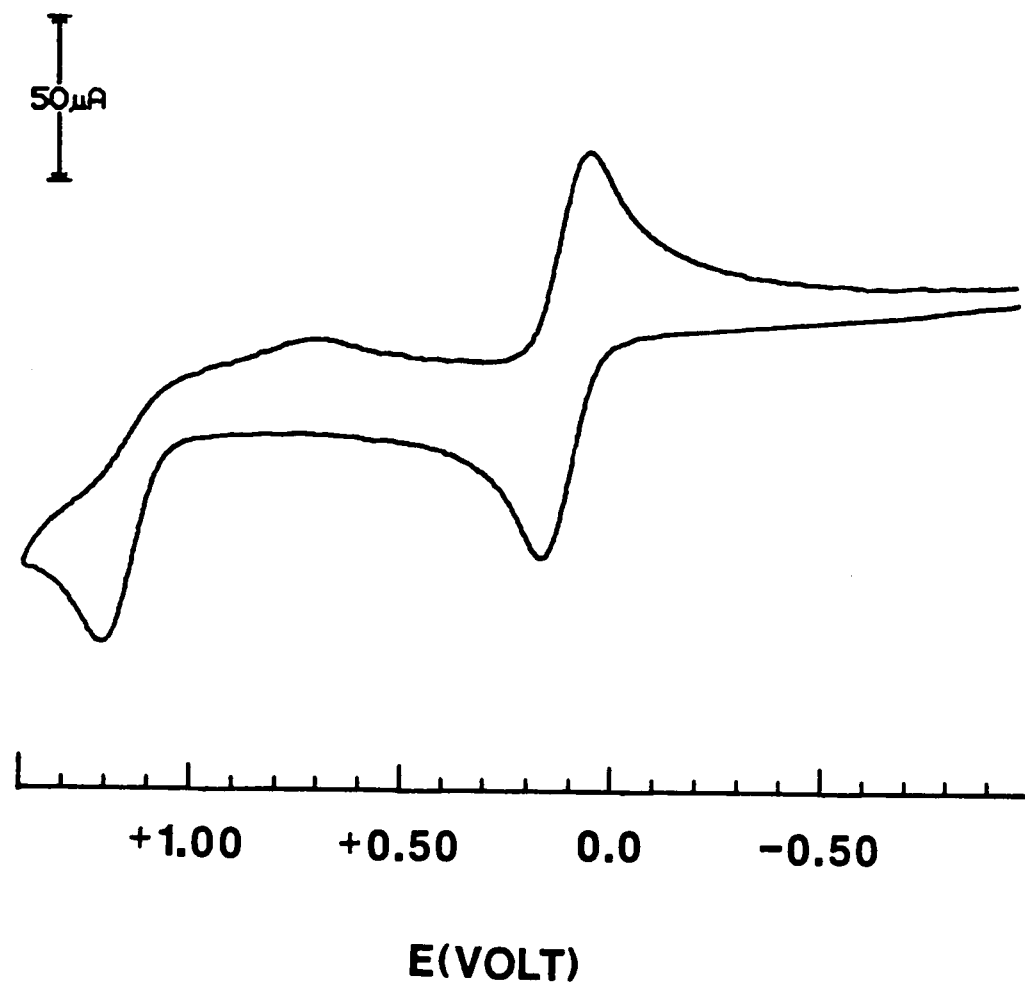


Figure 58. Cyclic voltammogram of 10^{-4} M $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{-mbPz})\}(\text{PF}_6)_2$, 60, in CH_2Cl_2 and 0.1 M TBAH.

TABLE XXVI

CYCLIC VOLTAMMETRIC DATA FOR COMPLEXES OF THE TYPE
 $([\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t-BuNC}})_2]_2(\mu\text{-Z}))(\text{PF}_6)_2$

Z	v ^a	E _{pa} , V	E _{pc} , V	ΔE, V	E _{1/2} , V	i _{pc} /i _{pa}
bPz, <u>59</u>	50	0.123	0.015	0.108	0.069	1.1
	100	0.124	0.007	0.117	0.066	1.1
	200	0.133	-0.004	0.137	0.065	1.1
	300	0.137	-0.016	0.153	0.061	1.1
	400	0.145	-0.019	0.164	0.063	1.1
	500	0.153	-0.021	0.174	0.066	1.1
mbPz, <u>60</u>	50	0.101	-0.020	0.121	0.041	1.1
	100	0.108	-0.026	0.134	0.041	1.1
	200	0.114	-0.042	0.156	0.036	1.1
	300	0.126	-0.049	0.175	0.039	1.1
	400	0.134	-0.053	0.187	0.041	1.1
	500	0.141	-0.056	0.197	0.043	1.1

^a Sweep rate in mV/s

Bulk electrolysis just past the first anodic wave of 59 and 60 generates stable-green paramagnetic solids, 61 and 62, respectively. The cyclic voltammograms of 59 before and after a two-electron bulk electrolysis are shown in Figure 59, and reveal no major differences. The cyclic voltammogram of 59 in a CH_2Cl_2 solution containing 0.1 M TBAH exhibits two anodic waves at +0.158 and +1.220 V, and cathodic waves at +0.854, and +0.29 V. The cyclic voltammogram after bulk electrolysis at +0.25 V reveals anodic waves at +0.13 and +1.25 V, and cathodic waves at +0.51 and -0.07 V. The IR spectra of 61 and 62 reveal CN bands between 2150 and 2170 cm^{-1} (Table XXVII), and PF_6^- bands at 839(s) and 557(m) cm^{-1} . The higher CN stretching frequencies observed for 61 and 62 are attributed to decreased back-bonding of the Rh d π electron density into the carbon π^* orbitals. The absence of CN bands in the vicinity where bands are usually observed for isocyanide bound to Rh(I) indicates that the rhodium atoms are in identical oxidation states, and that each dimeric unit was oxidized by one electron.

The UV-Vis and NIR data shown in Table XXVII are similar to that of the dinuclear Rh(1.5) pyrazolate compounds, 34-38. The UV-Vis spectra of 61 and 62 reveal a broad band at approximately 580 nm, and a band with a higher extinction coefficient around 431 nm. The NIR spectra of 61 and 62 show two overlapping bands between 850 and 1010 nm, whereas 59 and 60 do not absorb energy in the NIR region of the electromagnetic spectrum.

The room-temperature ESR spectra of 61 and 62 in CH_2Cl_2 exhibit isotropic signal at $g = 2.15$ indicative of a metal-based

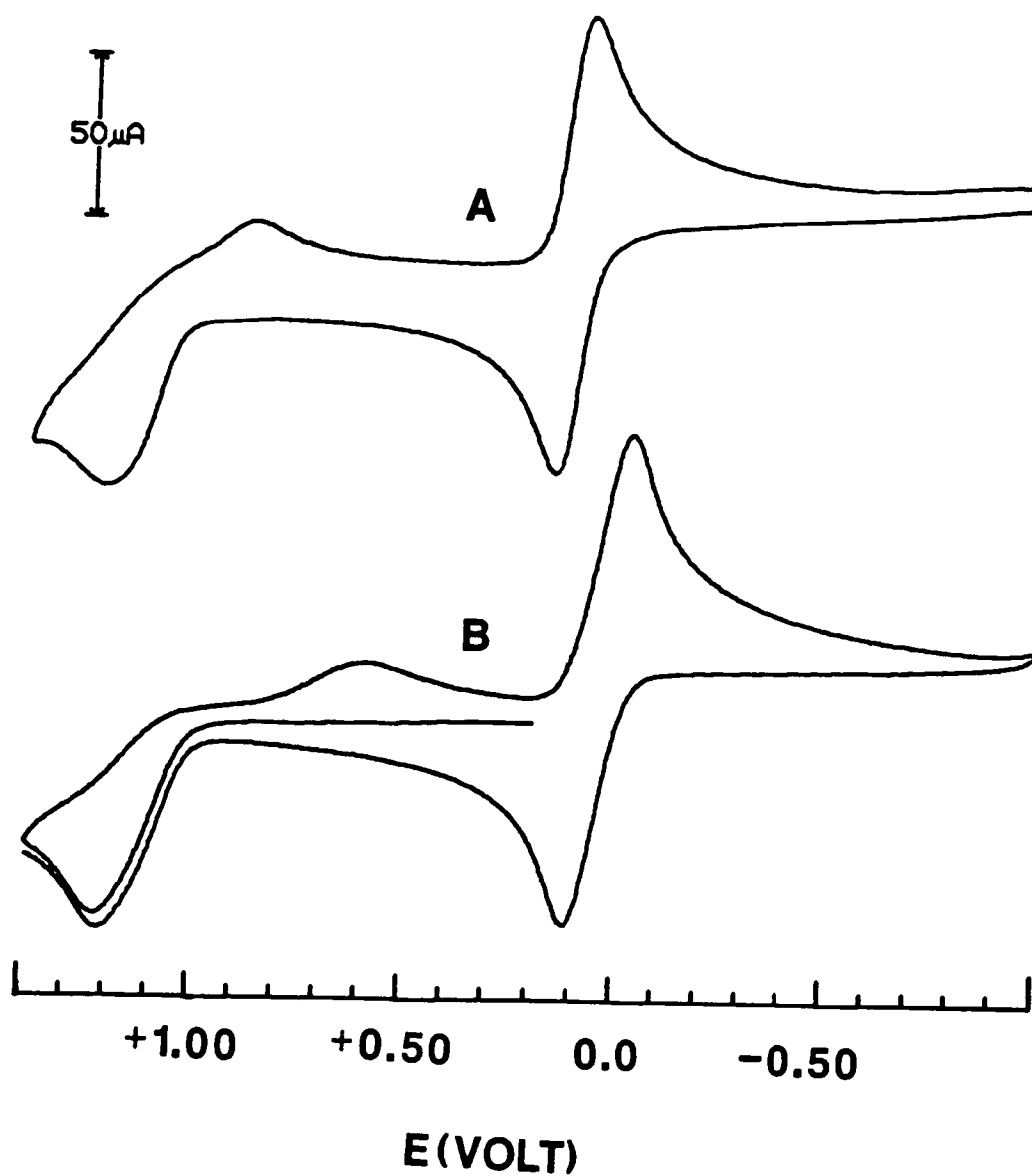


Figure 59. Cyclic voltammograms of 10^{-4} M $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{-bPz})\}(\text{PF}_6)_2$, 59, in CH_2Cl_2 and 0.1 M TBAH (A) before bulk oxidation, and (B) after bulk oxidation.

TABLE XXVII

UV-VIS, NIR, AND IR DATA FOR COMPLEXES OF THE TYPE
 $([\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{-Z}))(\text{PF}_6)_4$

Z	<u>UV-Vis</u>	<u>NIR</u>	<u>IR</u>
	$\lambda_{\text{max}}, \text{nm}(\epsilon)$	$\lambda_{\text{max}}, \text{nm}(\epsilon)$	$\nu(\text{CN}), \text{cm}^{-1}$
bPz, <u>61</u>	584(1,625)	990(1,200)	2164(s)
	437(33,100)	864(2,800)	2154(sh)
	387(5,100)		
mbPz, <u>62</u>	584(1,970)	1008(920)	2168(s)
	432(35,100)	865(1,900)	2156(sh)

unpaired electron. The observed line width of 82.25 G for compound 61 is approximately twice that observed for 62 (Table XXVIII) and the Rh(1.5) dimers. The broader line widths observed for 61 arise from the communication of the two metal-based unpaired electrons through the delocalized Π -system. The communication results in one electron affecting the spin state of the other electron, increasing the relaxation time of the electrons and thus a broader line width is observed. The anisotropic g-values of the polycrystalline samples at room-temperature are also consistent with the description of the unpaired electron in a metal-based orbital.

The frozen 4:1 CH₂Cl₂/toluene solution ESR spectra of 62 at -150 and -175 °C are shown in Figure 60A and B. The ESR behavior of 62 is similar to that of [Rh₂(μ -dapm)₂($\underline{t}$ -BuNC)₂(μ -345bPz)](PF₆)₂.⁸⁶ The ESR spectrum at -150 °C reveals the presence of two isomers, and at -175 °C, only one isomer. At -175 °C, the ESR spectrum of 62 exhibits three components at g-values of 2.07, 2.00 and 1.99 and is similar to the ESR spectrum of the thermochromic dinuclear Rh(1.5) complexes. The component at 2.07 exhibits a shoulder at g = 2.08. At -150 °C, a low-field signal is present in the ESR spectrum, with a g-value of 2.17. The signal at 2.17 indicates the formation of a second isomer. The two components at g-values of 2.07 and 2.00 are still present, with the component at g = 1.99 no longer defined.

The frozen 4:1 CH₂Cl₂/toluene solution ESR spectrum of 61 is shown in Figure 60. At -173 °C, the low-field signal appears to be an overlap of two components with g values near 2.24 and 2.18, and

TABLE XXVIII

ESR DATA FOR COMPLEXES OF THE TYPE
 $([\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{-Z}))(\text{PF}_6)_4$

Z	<u>Room temperature</u> ^a		<u>Frozen solution</u> ^b		
	g	Line width, G	High field g	Intermediate field g	Low field g
bPz, <u>61</u>	2.14	82.2	2.01 ^c 2.05 ^c		2.18 ^c 2.24 ^c
mbPz, <u>62</u>	2.15	43.8	2.00 ^d 1.99 ^d 2.00 ^e	2.07 ^d 2.08 ^d 2.07 ^e 2.08 ^e	 2.17 ^e

^a CH₂Cl₂ solution, ^b 4:1 CH₂Cl₂/toluene solution, ^c -173 °C,
^d -175 °C, ^e -150 °C.

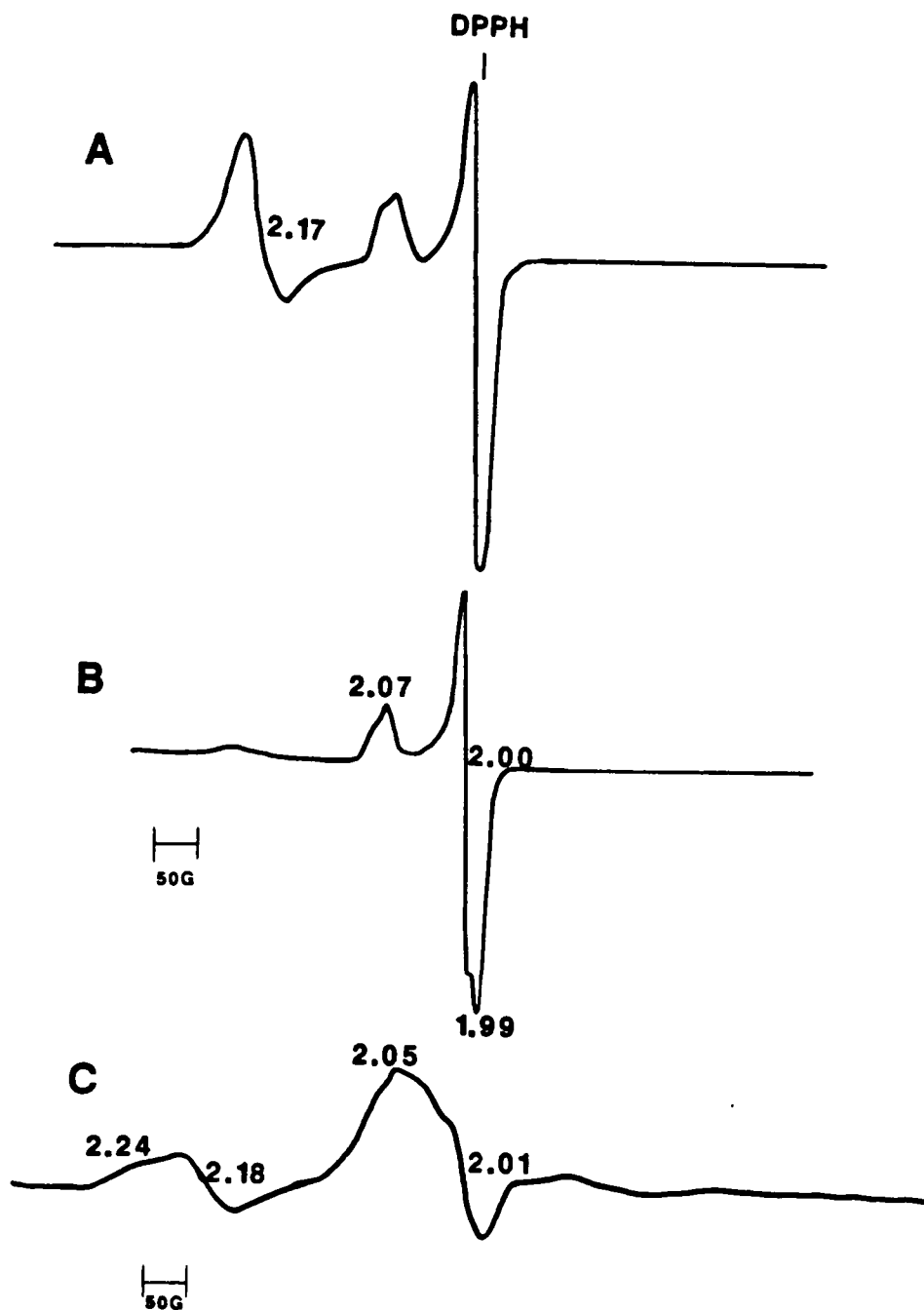


Figure 60. Frozen-solution ESR spectra of (A) $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{-mbPz})\}(\text{PF}_6)_4$, 62, at (A) -150°C , (B) -175°C , and (C) $\{[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2]_2(\mu\text{bPz})\}(\text{PF}_6)_4$, 61, at -173°C .

the high-field signal, likewise, appears to be a result of overlapping components with g-values of 2.05 and 2.01. The frozen solution ESR spectrum of 61 is consistent with the presence of two isomers. The low-field component at $g = 2.24$ occurs at a lower field than those observed for 62 and 38 at -150 and -196 °C, respectively.

The reactivity of the paramagnetic complexes, 61 and 62, include a disproportionation reaction followed by a proposed electron-transfer reaction in the presence of halide ions. Addition of one equivalent of Br^- to an acetone solution of 61 results in an instantaneous color change from green to orange. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum reveals a symmetrical AA'A''A'''XX' pattern with a chemical shift and $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 7.9 ppm and 92.8 Hz, respectively. These data are consistent with a dppm-Rh(II) complex. The NMR spectrum also reveals a broad phosphorus resonance in the base line between 19 and 22 ppm. Addition of a second equivalent of Br^- results in the appearance of an additional symmetrical pattern with a chemical shift and $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 20.0 ppm and 139.2 Hz. The chemical shift and $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ value of 20.0 ppm and 139.2 Hz are within experimental error of the values obtained for the parent compound, 59; while the values of 7.9 ppm and 92.8 Hz are similar to the $^{31}\text{P}\{\text{H}\}$ NMR data obtained from the brominated dinuclear Rh(II) complexes, 44-49. Similar results are obtained upon addition of chloride ions to 61. Chemical shifts of 20.0 ppm and 10.2 ppm with the corresponding $[\text{}^1\text{J}_{(\text{Rh-P})} + \text{}^x\text{J}_{(\text{Rh-P})}]$ values of 141.6 and 92.8 Hz are obtained from the $^{31}\text{P}\{\text{H}\}$ NMR spectra

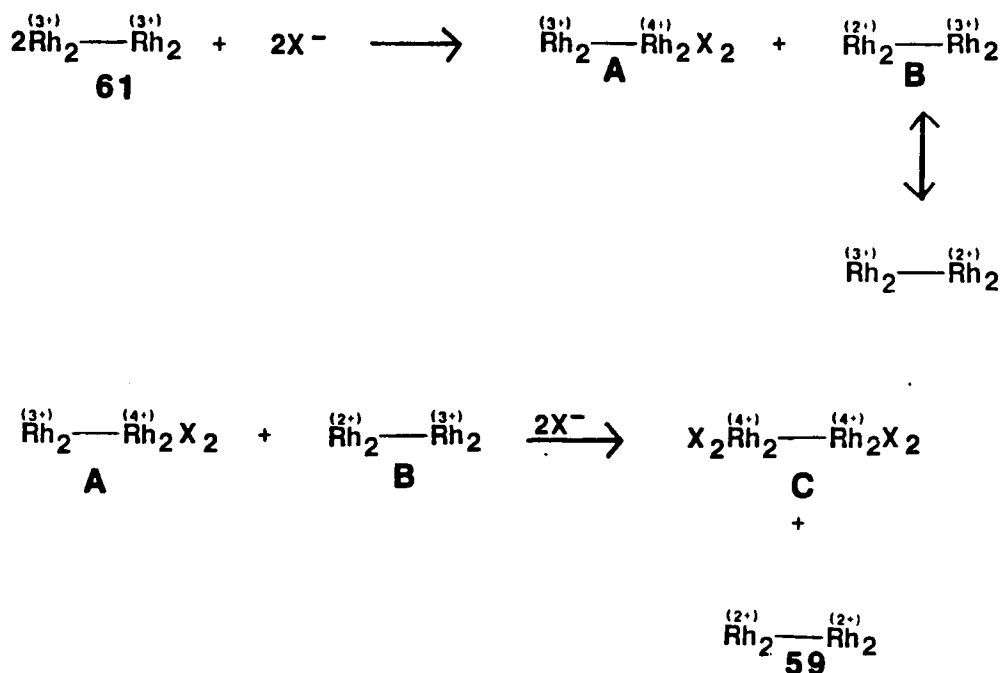
for the two symmetrical phosphorus resonances. The chemical shift of 10.2 ppm is similar to the chemical shift observed for the chlorinated dinuclear Rh(II) compound, 46.

The $^{31}\text{P(H)}$ NMR spectrum after the sequential addition of one equivalent of Br^- and Cl^- to 61 reveals three different types of phosphorus resonances. One of the phosphorus resonances corresponds to 59, while the other two symmetrical patterns have chemical shifts of 10.3 and 8.0 ppm. The formation of the two phosphorus units, with chemical shifts of 10.3 and 8.0 ppm and $[^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}]$ values of 92.8 Hz, correspond to the values obtained after two equivalents of chloride and bromide ions are added to 61, respectively.

Possible reactions that explain the above results are shown in Scheme V, and include a disproportionation reaction followed by an electron-transfer reaction.

The first reaction is a disproportionation reaction induced by a halide ion. The formation of A gives rise to the $^{31}\text{P(H)}$ NMR spectrum indicative of a Rh(II) complex. The mixed-valence dinuclear fragment joined to the halogenated dinuclear fragment contains a localized unpaired electron, and therefore does not affect the $^{31}\text{P(H)}$ NMR pattern of the adjoining dinuclear Rh(II) unit. The isomerization of B created by the delocalized Π system results in the absence of an observable phosphorus resonance ascribed to B. The species B could be stabilized through the delocalization of the electron density between the dinuclear Rh(I) and Rh(II) units such

Scheme V.



that upon addition of a second equivalent of halide ion the reaction preferentially occurs with A.

The addition of a second equivalent of halide ion results in an electron-transfer from complex A to B, with addition of halide to A generating C and 59. The formation of C and 59 results in the observed $^{31}\text{P(H)}$ NMR spectrum after the addition of two equivalents of halide ions.

The proposed attack of the second equivalent of halide ion on A instead of B is further substantiated by the sequential addition of two different halide ions. If the second equivalent of halide ion attacked B, two different phosphorus resonances might be expected for the two types of dinuclear Rh(I) units - one unit opposite a chlorinated dirhodium unit and the other opposite a

brominated dinuclear Rh(II) unit. The presence of only one type of dinuclear Rh(I) unit supports the proposed mechanism of a disproportionation reaction followed by an electron-transfer reaction.

With the exception of the observed $^{31}\text{P(H)}$ NMR pattern arising from the Rh(I) species, compound 62 also shows similar reactivity in the presence of halide ions. The addition of one equivalent of chloride ion to an acetone solution containing 62 results in an instantaneous color change from green to orange. The $^{31}\text{P(H)}$ NMR spectrum reveals an unsymmetrical pattern in the region where dinuclear dppm-Rh(II) complexes are usually observed. This pattern is similar to the typical AA'A''A'''XX' pattern except one of the major lines is split. The NMR spectrum also shows a broad phosphorus resonance in the base line between 17 and 21 ppm. The addition of a second equivalent of chloride ion produces a symmetrical phosphorus NMR pattern centered at 19.5 ppm where the broad resonance occurred. The pattern is identical to the $^{31}\text{P(H)}$ NMR pattern obtained after 23 was reduced by two electrons and then oxidized by two electrons in a $\text{CH}_3\text{CN/TBAH}$ solution. This observed pattern could be a consequence of the formation of two different types of dinuclear Rh(I) fragments, a coupling phenomenon, or a structural change. The other phosphorus resonance that was observed after the addition of the first equivalent of chloride ion does not reveal any splitting of major lines, and is typical of trans-dppm dinuclear rhodium complexes. A chemical shift and [$^1\text{J}_{(\text{Rh-P})} + ^x\text{J}_{(\text{Rh-P})}$] values of 10.1 ppm and 92.8 Hz are obtained from the $^{31}\text{P(H)}$ NMR spectrum for this Rh(II) complex. Further addition of

up to six equivalents of chloride ions results in no further alteration of the NMR spectrum. Similar results are obtained when Br^- or SCN^- are added to a solution containing 62.

The $^{31}\text{P}\{\text{H}\}$ NMR spectrum obtained from the bromide reaction gives a chemical shift and $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 7.8 ppm and 92.8 Hz for the Rh(II) complex, and a chemical shift of 19.5 ppm corresponding to the Rh(I) complex.

The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of the SCN^- induced reactions reveals a symmetrical pattern resembling an $\text{AA}'\text{A}''\text{A}''' \text{XX}'$ spin system of trans-dppm dinuclear rhodium complexes for the Rh(II) complex. The symmetrical patterns indicates that SCN^- is coordinating through either the sulfur or the nitrogen. The NMR spectrum gives a chemical shift and $[^1J_{(\text{Rh-P})} + ^xJ_{(\text{Rh-P})}]$ value of 10.7 ppm and 87.9 Hz for the Rh(II) complex, and a chemical shift of 19.7 ppm for the Rh(I) complex. The IR spectrum of an isolated product reveals CN bands at 2178(s), 2113(sh) and 2072(s) cm^{-1} . The band at 2178 cm^{-1} is assigned to the isocyanide ligand bound to a Rh(II) metal center, and the band at 2113 cm^{-1} is assigned to isocyanide ligand bound to a Rh(I) metal center. The broad CN band at 2072 cm^{-1} is between the stretching frequencies assigned for S and N bound SCN ligands in complexes 53-56 (Table XVII, page 211), and is in the region where the shoulder is observed in the CN stretch of 60. Therefore, a correct assignment of the CN band at 2072 cm^{-1} can not be made. The coordination of SCN^- through the sulfur or nitrogen atom is in contrast to the pyrazolate-bridged dinuclear Rh(II) complexes in which the thiocyanate ligands were determined to be coordinated

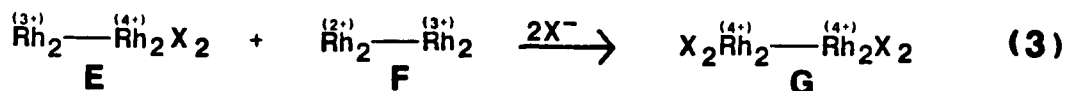
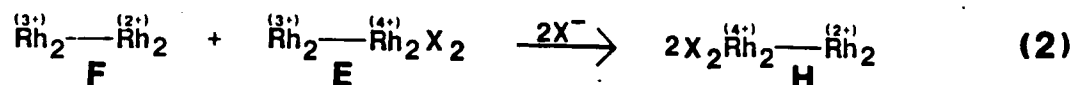
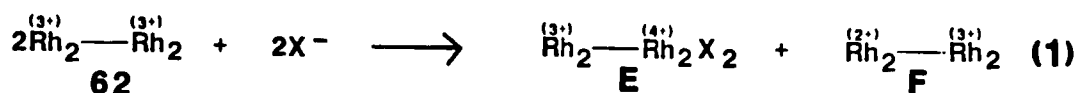
through both the sulfur and nitrogen atoms. The preference for sulfur or nitrogen-bound SCN^- ligands could arise from steric constraints imposed by the geometry of the tetrarhodium complex.

In an attempt to rationalize a mechanism for the reactions induced by anionic species, two different halide ions were added successively to 62. Addition of one equivalent of Cl^- to an acetone/ CH_2Cl_2 solution of 62 confirms the $^{31}\text{P}(\text{H})$ NMR results obtained earlier. The addition of one equivalent of Br^- to the 62/ Cl^- solution results in a $^{31}\text{P}(\text{H})$ NMR symmetrical pattern identical to that obtained earlier for dppm bound to $\text{Rh}(\text{I})$ and centered at 19.5 ppm. Phosphorus resonances are observed in the region where resonances are observed for dppm- $\text{Rh}(\text{II})$ complexes that were assigned to both the bromo and chloro $\text{Rh}(\text{II})$ complexes generated after the addition of Br^- and Cl^- to 62, respectively.

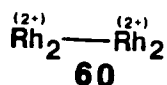
Phosphorus resonances for the $\text{Rh}(\text{I})$ complexes generated by the addition of SCN^- , Br^- , Cl^- and for the products obtained from the sequential addition of Cl^- and Br^- to 62, have identical chemical shifts within experimental error. This implies that in all cases the $\text{Rh}(\text{I})$ complexes are the same.

Possible mechanisms include disproportionation/electron-transfer reactions (Scheme VI) or a disproportionation/disproportionation reaction (Scheme VII). For the disproportionation/electron-transfer reactions, if the phosphorus resonance observed for dppm bound to $\text{Rh}(\text{I})$ arises from two different types of dinuclear $\text{Rh}(\text{I})$ fragments, such as for H and 60 in Scheme VI and VII, there should also be two different types of dinuclear $\text{Rh}(\text{II})$ fragments

Scheme VI.



+



(H and G in Scheme VI and VII). This is not observed. However, there is a possibility that the coupling in the dinuclear Rh(II) fragment in Structures G and H is not sensitive to the other dinuclear Rh₂-unit joined by the methylene bipyrazolate ligand, and either Scheme VI or VII would be consistent with the NMR data. If the phosphorus resonance observed for dppm bound to Rh(I) arises from one type of dinuclear Rh(I) fragment, only reactions (1) and (3) of Scheme VI would be applicable. This implies that a disproportionation of 62 followed by an electron transfer from E to F is occurring. An electron transfer from F to E (reaction (2)) is

CHAPTER VII

CONCLUSION

Although dirhodium complexes containing trans dppm and dppp bridging ligands undergo similar chemical and electrochemical reactions, steric and electronic factors of the transoid bridging ligand dictate the stability and behavior of the dirhodium complexes. It has been demonstrated that the two analogous compounds 9 and 14 show different reactivity and spectroscopic behavior. Compound 9, which is stable and fluxional on the time scale of NMR, adds a mole of CO to generate another stable complex, 11. This behavior is opposite that of the dppm analogue. Compound 14 has been demonstrated to lose a chloride ion in polar solvents and add a mole of CO which generates an unstable complex. Compound 14 is also non-fluxional on the time scale of NMR spectroscopy. The reactivity of 9 and 14 also differ in their reaction with t-BuNC. While a product can not be isolated from a reaction between 14 and t-BuNC, a product can be isolated from a reaction of 9 with t-BuNC.

The loss of a chloride ion from 14 generates 4. Compound 4 readily adds a mole of CO and under prolonged treatment of CO undergoes a reduction of the metal centers, generating 1. Compound 4 can also be electrochemically reduced by one or two electrons. The one-electron reduction generates 82 and 14 via an EC mechanism, while the two-electron reduction generates 82.

Investigations of A-frame complexes containing pyrazolate and substituted pyrazolates at the bridgehead position and terminal iso-

cyanide ligands have shown that these complexes undergo oxidative addition reactions with halogens. Unlike the dicarbonyl compounds, 18 and 19, chlorination and bromination do not halogenate the four position of the pyrazolate ring.

Compounds 24-29 have also been shown to react with a variety of acids. When the acid contains a coordinating anion, such as NO_3^- or CH_3COO^- , bis adducts are produced as the formal oxidation state of the rhodium atoms increases from +1 to +2. The reactions with H_2SO_4 in THF generate dinuclear $\text{Rh}(1.5)$ compounds, 34-38; but in methanol, a green solid is obtained from the reaction with 26 that is different from the product obtained in THF. This product has been shown to give $^{31}\text{P}(\text{H})$ and ^1H NMR spectra that are not broad, yet gives an anisotropic room-temperature ESR spectrum. The reactions with HClO_4 also appear to generate mixed-valence species that exhibit narrow-lined $^{31}\text{P}(\text{H})$ NMR spectra.

The electrochemical investigation of 18-20 and 22-29 reveals two consecutive one-electron oxidation waves; the first corresponds to a quasireversible and the second to an irreversible electron-transfer process. Stable paramagnetic species are obtained when bulk oxidation is performed between the two anodic waves. ESR spectroscopy has been used to determine that the unpaired electron is metal-based. The frozen solution ESR spectrum of 38 resembles that of $[\text{Rh}_2(\mu\text{-dppm})_2(\text{dimen})_2]^{3+}$ obtained by Boyd et al.²⁰ The ESR spectrum reveals a well-defined triplet attributed to coupling of the unpaired electron to two equivalent dirhodium atoms, a five line pattern attributed to hyperfine coupling to the four phosphorus

atoms, and a component assigned to the $\text{Rh}_2\text{N}_2\text{C}_2$ principal magnetic axis. However, for solutions of 34-37, a thermochromic effect is observed upon freezing to 77 K. The ESR spectra obtained are noticeably different with components at approximately $g = 2.06$, 2.00 and 1.99 . These spectra show no signs of coupling to the rhodium or phosphorus atoms, but the nature of the signal at approximately $g = 2.06$ does appear to depend on the pyrazolate. The frozen solution ESR spectra of 66-70 resemble that obtained for 38, and indicates a metal-based unpaired electron. The spectra of 66, 68 and 70 also reveals a signal at $g = 2.0$ which is attributed to the formation of another isomer. This isomer appears to be similar to the isomer formed from the frozen solution of 34-37.

A thermosolvent effect was also detected by ESR spectroscopy for 69. In a frozen solution of CH_2Cl_2 /ethanol, the ESR spectrum is similar to 34-37 at 77 K; and in a frozen solution of CH_2Cl_2 /toluene, the ESR spectrum is similar to 38 at 77 K.

The reactivity of the dinuclear $\text{Rh}(1.5)$ complexes include: (1) induced disproportionation reactions, and (2) electron-transfer reactions with dinuclear $\text{Rh}(\text{I})$ compounds whose anodic wave occurs at a less-positive potential than the cathodic wave of the dinuclear $\text{Rh}(1.5)$ compound.

The electrochemical behavior of 25 in the presence of neutral bases was investigated. It was determined that as the basicity of the coordinating species increases, the more the second oxidation wave shifts to less positive potentials. The non-dependence of the first oxidation wave with the different bases was also demonstrated.

Further electrochemical investigation showed that the halogenated dinuclear Rh(II) complexes can also be prepared electrochemically. The electrochemical generation of novel complexes was extended to include thiocyanate which coordinates to the rhodium atoms through the sulfur and nitrogen atoms. The formation of 40 from the oxidation of 24 in TBAH/CH₂Cl₂/TBAAc reveals two interesting points: (1) the possible reaction between acetate and CH₂Cl₂, and (2) the unprecedented folding of the methylene groups of the dppm ligands over the open site opposite the bridging pyrazolate ligand.

The investigation into tetranuclear rhodium complexes was initiated and has revealed interesting trends when compared to the dinuclear complexes. While the electrochemical behaviors of 57 and 58 do not parallel those of the dimeric rhodium complexes, 18-23, complexes 59 and 60 do appear to mimic the electrochemical behavior of the dimeric complexes 24-29 in CH₂Cl₂.

The cyclic voltammetric behavior of 59 and 60 in CH₂Cl₂ reveals two consecutive two-electron oxidation waves; a quasireversible wave followed by an irreversible wave. Stable-paramagnetic species were generated after bulk oxidation between the two anodic waves. Room-temperature ESR spectra reveal isotropic signals for which the line width of 61 is twice that of 62. Frozen solution ESR spectra reveal the presence of two isomers in each spectrum. One isomer results in ESR components that are indicative of trans-dppm metal-based unpaired electrons, and the second isomer results in ESR components that are similar to the ESR spectra obtained for 34-37 at 77 K. The reactivity of 61 and 62 includes a halide-

induced disproportionation reaction followed by a proposed electron-transfer reaction.

The major goal of this work was to investigate the effect of ligand modification on the chemical and electrochemical behavior of dinuclear rhodium complexes. The potential application of dinuclear rhodium complexes as homogeneous catalysts depends, in part, on their ability to undergo charge-transfer reactions. This work has shown that the σ donor and π acceptor capabilities of the terminal ligands affect the electrochemical potential at which the rhodium atoms are oxidized. This investigation has also demonstrated that the basicity of the bridgehead ligand and the nature of the trans-bridging ligands likewise affect the electron-transfer reactions of these complexes.

Although some progress on the chemical and electrochemical behavior of some dirhodium complexes was accomplished, further investigation is needed. Several aspects that warrant exploration are: (1) a determination of the electronic and/or structural changes that occur in the paramagnetic complexes which exhibit thermochromism, and (2) a resolution of the differences between the paramagnetic complexes obtained from the acid reactions and those obtained from bulk oxidation. One possibility would be to synthesize a complex in which the thermochromic effect occurs at higher temperatures in order to obtain further analytical data and perhaps a crystal structure. Two known facts that can lead to a good starting point for the synthesis of such a compound are that: (1) the thermochromic effect occurs at higher temperatures for dpam

complexes, and (2) electron-donating substituents on the pyrazolate ring increase the transition temperature.

Preliminary studies on the tetranuclear complexes have been initiated; however, further investigation into their chemical behavior is needed to determine the exact mechanism and products formed in the induced disproportionation/electron-transfer reactions. Investigation of their electrochemical behavior in the presence of coordinating species may also be of interest in determining what factors influence their redox chemistry.

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APPENDIXES

APPENDIX A

X-RAY DATA FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)$

CRYSTAL DATA FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)$

$\text{C}_{63}\text{H}_{65}\text{Cl}_2\text{F}_6\text{N}_4\text{P}_5\text{Rh}_2$

F. W. 1423.8095 $F(000) = 724$

Cu $K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$)

temperature = $22(1)^\circ\text{C}$

monoclinic space group $P2_1/c$

$\beta = 96.82(2)^\circ$

$a = 12.355(2) \text{ \AA}$, $b = 20.759(9) \text{ \AA}$, $c = 24.689(5) \text{ \AA}$

$V = 6287.4 \text{ \AA}^3$

$Z = 4$, $D(\text{calc}) = 1.648 \text{ g/cc}$

Abs. coeff. (μ) = 65.6 cm^{-1}

INTENSITY MEASUREMENTS FOR
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)$

Instrument:	Enraf-Nonius CAD4 diffractometer
Monochromator:	Graphite crystal, incident beam
Scan type:	ω - 2θ
Maximum θ :	67 °
No. of refl. measured:	11,200 total, 8080 unique
Corrections:	Lorentz-polarization Empirical Absorption

STRUCTURE SOLUTION AND REFINEMENT FOR
 $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)$

Solution:	Direct Methods
Hydrogen Atoms:	Calculated positions, refined isotropically
Refinement:	Full Matrix least-squares
Minimization function:	$w(F_o - F_c)$
Least-squares weights:	$1/[\sigma(F_o)]^2$
Parameters refined:	740
Unweighted agreement factor, R	0.045
Weighted agreement factor, R_w	0.059
Convergence, largest shift	0.33
Computer hardware:	MicroVax II
Computer software:	SDPVAX (Enraf-Nonius)

BOND DISTANCES FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)$

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
Rh(1)	Rh(2)	2.7678(6)	P(5)	F(3)	1.506(8)
Rh(1)	P(11)	2.345(1)	P(5)	F(4)	1.42(1)
Rh(1)	P(12)	2.340(1)	P(5)	F(5)	1.438(8)
Rh(1)	Cl(1)	2.489(1)	P(5)	F(6)	1.270(8)
Rh(1)	C(11)	1.933(5)	C(111)	C(112)	1.385(8)
Rh(1)	N(1)	2.069(5)	C(111)	C(116)	1.404(8)
Rh(2)	P(21)	2.377(1)	C(112)	C(113)	1.385(9)
Rh(2)	P(22)	2.383(1)	C(113)	C(114)	1.378(9)
Rh(2)	Cl(2)	2.471(1)	C(114)	C(115)	1.39(1)
Rh(2)	C(21)	1.940(5)	C(115)	C(116)	1.391(9)
Rh(2)	N(2)	2.067(5)	C(111')	C(112')	1.38(1)
P(11)	C(1)	1.834(5)	C(111')	C(116')	1.36(1)
P(11)	C(111)	1.814(5)	C(112')	C(113')	1.39(1)
P(11)	C(111')	1.829(5)	C(113')	C(114')	1.38(1)
P(12)	C(2)	1.832(5)	C(114')	C(115')	1.35(1)
P(12)	C(121)	1.837(6)	C(115')	C(116')	1.41(1)
P(12)	C(121')	1.823(6)	C(121)	C(122)	1.366(9)
P(21)	C(1)	1.807(4)	C(121)	C(126)	1.371(9)
P(21)	C(211)	1.822(5)	C(122)	C(123)	1.39(1)
P(22)	C(211')	1.839(5)	C(123)	C(124)	1.32(1)
P(22)	C(2)	1.828(6)	C(124)	C(125)	1.37(1)
P(22)	C(221)	1.830(5)	C(125)	C(126)	1.39(1)
P(22)	C(221')	1.837(6)	C(121')	C(122')	1.39(1)
P(5)	F(1)	1.531(7)	C(121')	C(126')	1.358(9)

Bond distances in Angstroms.

BOND DISTANCES (Continued)

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
P(5)	F(2)	1.505(7)	C(122')	C(123')	1.41(1)
C(123')	C(124')	1.34(1)	C(221')	C(222')	1.372(8)
C(124')	C(125')	1.37(1)	C(221')	C(226')	1.401(9)
C(125')	C(126')	1.39(1)	C(222')	C(223')	1.399(9)
C(211)	C(212)	1.378(9)	C(223')	C(224')	1.38(1)
C(211)	C(216)	1.378(9)	C(224')	C(225')	1.37(1)
C(212)	C(213)	1.40(1)	C(225')	C(226')	1.39(1)
C(213)	C(214)	1.35(1)	C(21)	N(22)	1.154(7)
C(214)	C(215)	1.34(1)	N(22)	C(23)	1.475(7)
C(215)	C(216)	1.43(1)	C(23)	C(24)	1.51(1)
C(211')	C(212')	1.378(8)	C(23)	C(25)	1.52(1)
C(211')	C(216')	1.395(8)	C(23)	C(26)	1.51(1)
C(212')	C(213')	1.38(1)	C(11)	N(12)	1.140(7)
C(213')	C(214')	1.384(9)	N(12)	C(13)	1.464(8)
C(214')	C(215')	1.348(9)	C(13)	C(14)	1.50(1)
C(215')	C(216')	1.39(1)	C(13)	C(15)	1.50(1)
C(221)	C(222)	1.389(9)	C(13)	C(16)	1.49(1)
C(221)	C(226)	1.382(8)	N(1)	N(2)	1.350(6)
N(1)	C(5)	1.331(7)	N(2)	C(3)	1.342(7)
C(222)	C(223)	1.40(1)	C(3)	C(4)	1.389(7)
C(223)	C(224)	1.37(1)	C(4)	C(5)	1.383(9)
C(224)	C(225)	1.36(1)	C(225)	C(226)	1.393(9)

Bond distances in Angstroms.

BOND ANGLES FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2\text{Cl}_2(\mu\text{-Pz})](\text{PF}_6)$

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
Rh(2)	Rh(1)	P(11)	94.14(3)	P(22)	Rh(2)	C(21)	88.4(1)
Rh(2)	Rh(1)	P(12)	96.38(3)	P(22)	Rh(2)	N(2)	96.4(1)
Rh(2)	Rh(1)	Cl(1)	157.05(3)	Cl(2)	Rh(2)	C(21)	92.5(2)
Rh(2)	Rh(1)	C(11)	96.7(1)	Cl(2)	Rh(2)	N(2)	92.2(1)
Rh(2)	Rh(1)	N(1)	70.0(1)	C(21)	Rh(2)	N(2)	173.5(2)
P(11)	Rh(1)	P(12)	167.75(5)	Rh(1)	P(11)	C(1)	113.0(2)
P(11)	Rh(1)	Cl(1)	86.79(5)	Rh(1)	P(11)	C(111)	112.5(2)
P(11)	Rh(1)	C(11)	87.8(1)	Rh(1)	P(11)	C(111')	117.7(2)
P(11)	Rh(1)	N(1)	96.8(1)	C(1)	P(11)	C(111)	102.3(2)
P(12)	Rh(1)	Cl(1)	85.96(5)	C(1)	P(11)	C(111')	107.3(3)
P(12)	Rh(1)	C(11)	84.8(2)	C(111)	P(11)	C(111')	102.4(2)
P(12)	Rh(1)	N(1)	92.6(1)	Rh(1)	P(12)	C(2)	108.5(2)
Cl(1)	Rh(1)	C(11)	106.3(1)	Rh(1)	P(12)	C(121)	115.9(2)
Cl(1)	Rh(1)	N(1)	87.1(1)	Rh(1)	P(12)	C(121')	118.6(2)
C(11)	Rh(1)	N(1)	166.2(2)	C(2)	P(12)	C(121)	100.3(3)
Rh(1)	Rh(2)	P(21)	93.25(3)	C(2)	P(12)	C(121')	108.1(3)
Rh(1)	Rh(2)	P(22)	90.94(3)	C(121)	P(12)	C(121')	103.8(3)
Rh(1)	Rh(2)	Cl(2)	161.52(4)	Rh(2)	P(21)	C(1)	110.1(2)
Rh(1)	Rh(2)	C(21)	105.9(2)	Rh(2)	P(21)	C(211)	117.6(2)
Rh(1)	Rh(2)	N(2)	69.8(1)	Rh(2)	P(21)	C(211')	118.1(1)

Bond angles in degrees.

BOND ANGLES (Continued)

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
P(21)	Rh(2)	P(22)	173.85(4)	C(1)	P(21)	C(211)	108.3(2)
P(21)	Rh(2)	Cl(2)	90.38(5)	C(1)	P(21)	C(211')	101.3(2)
P(21)	Rh(2)	C(21)	86.1(1)	C(211)	P(21)	C(211')	99.6(2)
P(21)	Rh(2)	N(2)	89.3(1)	Rh(2)	P(22)	C(2)	114.4(2)
P(22)	Rh(2)	Cl(2)	87.06(5)	Rh(2)	P(22)	C(221)	114.1(2)
Rh(2)	P(22)	C(221')	121.2(2)	C(112)	C(113)	C(114)	120.8(7)
C(2)	P(22)	C(221)	101.4(2)	C(113)	C(114)	C(115)	119.3(6)
C(2)	P(22)	C(221')	103.1(3)	C(114)	C(115)	C(116)	119.8(6)
C(221)	P(22)	C(221')	99.9(2)	C(111)	C(116)	C(115)	121.2(6)
F(1)	P(5)	F(2)	177.8(5)	P(11)	C(111')	C(112')	118.8(5)
F(1)	P(5)	F(3)	90.5(4)	P(11)	C(111')	C(116')	121.8(5)
F(1)	P(5)	F(4)	88.0(7)	C(112')	C(111')	C(116')	119.4(6)
F(1)	P(5)	F(5)	87.8(4)	C(111')	C(112')	C(113')	120.7(7)
F(1)	P(5)	F(6)	90.8(7)	C(112')	C(113')	C(114')	119.0(8)
F(2)	P(5)	F(3)	90.8(4)	C(113')	C(114')	C(115')	121.0(8)
F(2)	P(5)	F(4)	90.3(6)	C(114')	C(115')	C(116')	119.9(9)
F(2)	P(5)	F(5)	90.8(4)	C(111')	C(116')	C(115')	120.0(7)
F(2)	P(5)	F(6)	91.1(7)	P(12)	C(121)	C(122)	120.7(5)
F(3)	P(5)	F(4)	81.8(7)	P(12)	C(121)	C(126)	122.3(5)
F(3)	P(5)	F(5)	175.9(7)	C(122)	C(121)	C(126)	116.9(6)
F(3)	P(5)	F(6)	90.8(8)	C(121)	C(122)	C(123)	121.3(7)

Bond angles in degrees

BOND ANGLES (Continued)

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
F(4)	P(5)	F(5)	94.4(8)	C(122)	C(123)	C(124)	121.3(8)
F(4)	P(5)	F(6)	172.5(8)	C(123)	C(124)	C(125)	119.0(8)
F(5)	P(5)	F(6)	92.9(8)	C(124)	C(125)	C(126)	120.0(7)
P(11)	C(1)	P(21)	116.9(3)	C(121)	C(126)	C(125)	121.2(7)
P(12)	C(2)	P(22)	115.1(3)	P(12)	C(121')	C(122')	120.5(5)
P(11)	C(111)	C(112)	124.4(4)	P(12)	C(121')	C(126')	120.6(5)
P(11)	C(111)	C(116)	117.9(4)	C(122')	C(121')	C(126')	118.8(6)
C(112)	C(111)	C(116)	117.7(5)	C(121')	C(122')	C(123')	118.4(8)
C(111)	C(112)	C(113)	121.2(6)	C(122')	C(123')	C(124')	122.3(9)
C(123')	C(124')	C(125')	119.0(8)	C(224)	C(225)	C(226)	120.1(7)
C(124')	C(125')	C(126')	119.7(7)	C(221)	C(226)	C(225)	120.9(6)
C(121')	C(126')	C(125')	121.6(6)	P(22)	C(221')	C(222')	122.8(5)
P(21)	C(211)	C(212)	118.1(5)	P(22)	C(221')	C(226')	118.1(4)
P(21)	C(211)	C(216)	122.0(5)	C(222')	C(221')	C(226')	119.1(6)
C(212)	C(211)	C(216)	119.4(6)	C(221')	C(222')	C(223')	120.1(6)
C(211)	C(212)	C(213)	120.5(6)	C(222')	C(223')	C(224')	120.5(6)
C(212)	C(213)	C(214)	120.1(7)	C(223')	C(224')	C(225')	119.4(7)
C(213)	C(214)	C(215)	120.2(8)	C(224')	C(225')	C(226')	120.8(6)
C(214)	C(215)	C(216)	121.5(8)	C(221')	C(226')	C(225')	119.9(6)
C(211)	C(216)	C(215)	118.1(7)	Rh(2)	C(21)	N(22)	172.8(5)
P(21)	C(211')	C(212')	120.3(4)	C(21)	N(22)	C(23)	171.0(7)

Bond angles in degrees.

BOND ANGLES (Continued)

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
P(21)	C(211')	C(216')	121.4(4)	N(22)	C(23)	C(24)	107.0(6)
C(212')	C(211')	C(216')	117.8(5)	N(22)	C(23)	C(25)	107.5(5)
C(211')	C(212')	C(213')	121.0(6)	N(22)	C(23)	C(26)	108.6(5)
C(212')	C(213')	C(214')	120.7(6)	C(24)	C(23)	C(25)	109.3(7)
C(213')	C(214')	C(215')	118.7(5)	C(24)	C(23)	C(26)	112.2(7)
C(214')	C(215')	C(216')	121.6(6)	C(25)	C(23)	C(26)	112.0(7)
C(211')	C(216')	C(215')	120.2(6)	Rh(1)	C(11)	N(12)	176.3(4)
P(22)	C(221)	C(222)	117.4(4)	C(11)	N(12)	C(13)	179.1(5)
P(22)	C(221)	C(226)	123.5(4)	N(12)	C(13)	C(14)	107.0(7)
C(222)	C(221)	C(226)	118.9(5)	N(12)	C(13)	C(15)	106.2(6)
C(221)	C(222)	C(223)	119.2(6)	N(12)	C(13)	C(16)	106.9(6)
C(222)	C(223)	C(224)	121.1(7)	C(14)	C(13)	C(15)	110.2(8)
C(223)	C(224)	C(225)	119.7(7)	C(14)	C(13)	C(16)	112.1(7)
C(15)	C(13)	C(16)	113.9(7)	Rh(2)	N(2)	N(1)	110.3(3)
Rh(1)	N(1)	N(2)	109.6(3)	Rh(2)	N(2)	C(3)	141.4(4)
Rh(1)	N(1)	C(5)	141.3(4)	N(1)	N(2)	C(3)	108.0(5)
N(2)	N(1)	C(5)	109.0(4)	N(2)	C(3)	C(4)	109.0(5)
C(3)	C(4)	C(5)	105.0(5)	N(1)	C(5)	C(4)	109.1(5)

Bond angles in degrees.

POSITIONAL PARAMETERS ($\times 10^4$) AND THEIR STANDARD DEVIATIONS
FOR NON-HYDROGEN ATOMS

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>U</u>
Rh(1)	2863.5(3)	2817.9(2)	1705.5(1)	2.308(6)
Rh(2)	3063.2(3)	1646.7(2)	1190.9(1)	2.300(6)
P(11)	4688.7(11)	3108.7(6)	1673.5(5)	2.39(2)
P(12)	976.6(11)	2764.9(6)	1724.4(5)	2.66(2)
P(21)	4994.7(11)	1717.0(6)	1259.9(5)	2.43(2)
P(22)	1131.8(11)	1544.7(6)	1021.9(5)	2.63(2)
Cl(1)	2876.3(12)	3581.3(6)	2483.5(5)	3.58(3)
Cl(2)	3155.8(12)	475.0(6)	1026.8(6)	3.88(3)
P(5)	7508.6(12)	1572.6(9)	4602.2(9)	5.43(4)
F(1)	7635(8)	2215(3)	4312(3)	15.7(3)
F(2)	7341(7)	938(3)	4875(3)	15.7(2)
F(3)	7690(10)	1904(4)	5148(3)	19.9(4)
F(4)	6412(7)	1747(6)	4646(6)	25.2(5)
F(5)	7265(11)	1282(4)	4073(3)	23.8(5)
F(6)	8603(6)	1455(7)	4618(6)	28.0(6)
C(1)	5414(4)	2551(2)	1267(2)	3.1(1)
C(2)	383(5)	2280(3)	1144(2)	3.3(1)
C(111)	4823(4)	3870(2)	1327(2)	2.9(1)
C(112)	5497(5)	3970(3)	925(2)	3.9(1)
C(113)	5604(5)	4574(3)	699(3)	4.5(1)
C(114)	5043(6)	5095(3)	870(3)	4.7(1)
C(115)	4360(6)	5010(3)	1273(3)	4.5(1)

POSITIONAL PARAMETERS (Continued)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>U</u>
C(116)	4247(5)	4402(3)	1495(2)	3.8(1)
C(111')	5545(5)	3232(3)	2322(2)	3.5(1)
C(112')	5589(6)	2754(4)	2713(3)	5.3(2)
C(113')	6183(6)	2841(5)	3221(3)	7.1(2)
C(114')	6727(8)	3414(5)	3332(3)	8.5(3)
C(115')	6688(9)	3886(5)	2956(4)	9.9(3)
C(116')	6101(7)	3792(4)	2437(3)	7.4(2)
C(121)	228(5)	3523(3)	1585(2)	3.7(1)
C(122)	-853(6)	3519(4)	1388(4)	7.9(2)
C(123)	-1428(7)	4088(4)	1279(5)	9.5(3)
C(124)	-979(7)	4654(4)	1407(4)	6.8(2)
C(125)	107(7)	4680(4)	1604(4)	7.4(2)
C(126)	703(6)	4113(3)	1694(4)	6.1(2)
C(121')	464(5)	2458(3)	2337(2)	2.6(1)
C(122')	-138(7)	2851(4)	2643(3)	6.8(2)
C(123')	-500(8)	2595(5)	3118(3)	8.2(2)
C(124')	-236(6)	2002(5)	3297(3)	6.5(2)
C(125')	364(6)	1615(4)	2994(3)	5.8(2)
C(126')	709(6)	1851(3)	2516(2)	4.6(1)
C(211)	5779(5)	1307(3)	1830(2)	3.6(1)
C(212)	5562(6)	666(3)	1913(3)	4.9(1)
C(213)	6227(6)	306(4)	2301(3)	6.0(2)
C(214)	7055(7)	592(4)	2615(3)	7.3(2)
C(215)	7275(7)	1217(5)	32544(4)	7.8(2)

POSITIONAL PARAMETERS (Continued)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>U</u>
C(216)	6658(6)	1593(4)	2133(3)	5.6(2)
C(211')	5679(4)	1397(2)	695(2)	3.0(1)
C(212')	5628(5)	749(3)	573(3)	4.8(1)
C(213')	6208(6)	493(3)	179(3)	5.3(2)
C(214')	6893(5)	877(3)	-87(3)	4.5(1)
C(215')	6959(5)	1510(3)	35(3)	5.2(1)
C(216')	6369(5)	1780(3)	423(3)	4.9(1)
C(221)	622(4)	1373(3)	310(2)	3.2(1)
C(222)	896(7)	783(3)	99(3)	5.2(2)
C(223)	453(8)	612(3)	-428(3)	6.3(2)
C(224)	-238(6)	1019(4)	-741(3)	5.9(2)
C(225)	-500(6)	1598(4)	-537(3)	5.0(2)
C(226)	-74(5)	1777(3)	-11(2)	4.2(1)
C(221')	401(5)	922(3)	1363(2)	3.7(1)
C(222')	924(5)	470(3)	1705(2)	4.1(1)
C(223')	320(6)	17(3)	1962(3)	5.4(2)
C(224')	-802(6)	10(4)	1865(3)	6.0(2)
C(225')	-1323(5)	448(4)	1512(3)	5.5(2)
C(226')	-739(5)	909(3)	1262(3)	4.4(1)
C(21)	3076(4)	1845(3)	424(2)	3.0(1)
N(22)	3148(4)	1905(3)	-35(2)	3.8(1)
C(23)	3300(5)	1876(4)	-618(2)	4.6(1)
C(24)	3670(10)	1201(5)	-730(4)	10.2(3)
C(25)	4195(7)	2348(5)	-711(3)	8.4(2)

POSITIONAL PARAMETERS (Continued)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>U</u>
C(26)	2235(7)	2043(5)	-951(3)	7.8(2)
C(11)	2500(4)	3322(2)	1051(2)	2.9(1)
N(12)	2234(4)	3601(2)	660(2)	3.9(1)
C(13)	1889(6)	3968(3)	163(3)	5.2(2)
C(14)	1369(10)	4578(5)	335(5)	11.8(3)
C(15)	1061(9)	3560(6)	-171(4)	11.6(3)
C(16)	2887(8)	4098(5)	-104(4)	9.8(3)
N(1)	3157(4)	2094(2)	2280(2)	3.04(9)
N(2)	3177(4)	1519(2)	2026(2)	2.94(8)
C(3)	3354(5)	1061(3)	2410(2)	3.7(1)
C(4)	3436(6)	1349(3)	2921(2)	4.6(1)
C(5)	3296(5)	2000(3)	2817(2)	3.8(1)

POSITIONAL PARAMETERS AND THEIR STANDARD DEVIATIONS
FOR HYDROGEN ATOMS

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>U x 10⁻³</u>
H(1A)	0.6244	0.2568	0.1420	39
H(1B)	0.5311	0.2717	0.0862	39
H(2A)	0.0347	0.2567	0.0792	42
H(2B)	-0.0410	0.2148	0.1213	42
H(122)	-0.1238	0.3098	0.1321	100
H(123)	-0.2197	0.4069	0.1100	120
H(124)	-0.1423	0.5057	0.1361	86
H(125)	0.0470	0.5106	0.1683	94
H(126)	0.1492	0.4137	0.1841	77
H(122')	-0.0311	0.3305	0.2529	86
H(123')	-0.0971	0.2867	0.3329	104
H(124')	-0.0472	0.1842	0.3647	82
H(125')	0.0552	0.1165	0.3117	73
H(126')	0.1148	0.1567	0.2299	58
H(112)	0.5914	0.3599	0.0795	49
H(113)	0.6094	0.4633	0.0408	57
H(114)	0.5126	0.5530	0.0706	60
H(115)	0.3951	0.5385	0.1402	57
H(116)	0.3746	0.4343	0.1782	48
H(112')	0.5188	0.2341	0.2629	67
H(113')	0.6216	0.2493	0.3502	90
H(114')	0.7157	0.3480	0.3697	108

POSITIONAL PARAMETERS (Continued)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>U x 10⁻³</u>
H(115')	0.7075	0.4303	0.3045	125
H(116')	0.6092	0.4136	0.2153	94
H(212)	0.4925	0.0456	0.1695	62
H(213)	0.6086	-0.0164	0.2345	76
H(214)	0.7508	0.0338	0.2902	92
H(215)	0.7885	0.1424	0.2785	99
H(216)	0.6858	0.2051	0.2067	71
H(212')	0.5164	0.0460	0.0773	61
H(213')	0.6132	0.0025	0.0085	67
H(214')	0.7330	0.0689	-0.0364	57
H(215')	0.7445	0.1792	-0.0159	66
H(216')	0.6439	0.2250	0.0508	62
H(222)	0.1404	0.0484	0.0322	66
H(223)	0.0643	0.0186	-0.0580	80
H(224)	-0.0547	0.0889	-0.1118	75
H(225)	-0.1000	0.1897	-0.0765	63
H(226)	-0.0275	0.2204	0.0136	53
H(222')	0.1738	0.0464	0.1771	52
H(223')	0.0705	-0.0304	0.2218	68
H(224')	-0.1231	-0.0313	0.2051	76
H(225')	-0.2136	0.0436	0.1433	70
H(226')	-0.1131	0.1232	0.1010	56
H(3)	0.3417	0.0589	0.2340	47
H(4)	0.3568	0.1133	0.3285	58

POSITIONAL PARAMETERS (Continued)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>U x 10⁻³</u>
H(5)	0.3299	0.2345	0.3100	48
H(24A)	0.3788	0.1160	-0.1143	129
H(24B)	0.4406	0.1104	-0.0485	129
H(24C)	0.3074	0.0870	-0.0640	129
H(25A)	0.4324	0.2339	-0.1124	106
H(25b)	0.3964	0.2814	-0.0606	106
H(25)	0.4918	0.2218	-0.0468	106
H(26A)	0.2331	0.2024	-0.1368	99
H(26B)	0.1635	0.1712	-0.0867	99
H(26C)	0.1998	0.2509	-0.0850	99
H(14A)	0.1109	0.4856	-0.0011	149
H(14B)	0.0696	0.4463	0.0539	149
H(14C)	0.1939	0.4841	0.0597	149
H(15A)	0.0784	0.3801	-0.0535	147
H(15B)	0.1418	0.3120	-0.0263	147
H(15C)	0.0401	0.3472	0.0050	147
H(16A)	0.2676	0.4362	-0.0464	124
H(16B)	0.3443	0.4364	0.0162	124
H(16C)	0.3245	0.3660	-0.0198	124

APPENDIX B

X-RAY DATA FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\underline{\text{t}}\text{-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$

CRYSTAL DATA FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$

Rh P F N C H
2 6 12 4 65 69

F.W. 1525.94 F(000) = 6200

crystal dimensions: 0.40 x 0.30 x 0.50 mm

peak width at half-height = 0.95

Cu K α radiation (λ = 1.54184 Å)

temperature = 23($\pm$ 1)°C

tetragonal space group I -4 2 d

a = 21.802 ($\pm$ 0) Å c = 30.635 ($\pm$ 3) Å

V = 14562.4 Å³

Z = 8 D(calc) = 1.39 g/cc

abs. coeff. (μ) = 56.3 cm⁻¹

INTENSITY MEASUREMENTS FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$

Instrument:	Enraf-Nonius CAD4 diffractometer
Monochromator:	Graphite crystal, incident beam
Attenuator:	Ni foil, factor 18.0
Take-off angle:	2.8°
Detector aperture:	4.0 to 5.9 mm horizontal 4.0 mm vertical
Crystal-detector dist.:	21 cm
Scan type:	ω -2 θ
Scan rate:	4 - 16.5 °/min (in ω)
Scan width, deg:	$0.8 + 0.140 \tan \theta$
Maximum 2 θ :	100.0°
No. of refl. measured:	4423 total, 3070 unique
Corrections:	Lorentz-polarization Reflection averaging (agreement on I = 2.0%) Empirical absorption (from 0.69 to 1.00 on I) Extinction (coefficient = 0.0000003)

STRUCTURE SOLUTION AND REFINEMENT FOR
[Rh₂(μ-dppm)₂(t-BuNC)₂(μ-35MPz)](PF₆)₂

Solution:	Patterson method
Hydrogen atoms:	Refined with Biso = 4.0 Å
Refinement:	Full matrix least-squares
Minimization function:	w(Fo - Fc)
Least-squares weights:	1 / [σ(Fo)] ²
Anomalous dispersion:	All non-hydrogen atoms
Reflections included:	1822 with Fo ² >3.0σ(Fo ²)
Parameters refined:	503
Unweighted agreement factor:	0.029
Weighted agreement factor:	0.037
Esd of obs. of unit weight:	1.12
Convergence, largest shift:	0.10 σ
High peak in final diff. map:	0.43(±4) e/Å ³
Computer hardware:	MicroVAX II
Computer software:	SDPVAX (Enraf-Nonius)

BOND DISTANCES FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$

Atom 1 =====	Atom 2 =====	Distance =====	Atom 1 =====	Atom 2 =====	Distance =====
Rh	P1	2.300(2)	C7	C8	1.38(1)
Rh	P2	2.351(2)	C7	C12	1.40(1)
Rh	N1	2.071(4)	C8	C9	1.40(1)
Rh	C25	1.928(7)	C9	C10	1.36(2)
P1	C13	1.799(8)	C10	C11	1.38(2)
P1	C19	1.814(7)	C11	C12	1.40(1)
P1	C33	1.850(8)	C13	C14	1.37(1)
P2	C1	1.825(6)	C13	C18	1.37(1)
P2	C7	1.841(9)	C14	C15	1.38(1)
P3	F1	1.581(5)	C15	C16	1.33(2)
P3	F2	1.579(7)	C16	C17	1.39(2)
P3	F3	1.565(5)	C17	C18	1.38(1)
P3	F4	1.579(5)	C19	C20	1.35(1)
P3	F5	1.576(5)	C19	C24	1.40(1)
P3	F6	1.590(6)	C20	C21	1.37(1)
N1	C30	1.347(7)	C21	C22	1.37(1)
N2	C25	1.149(8)	C22	C23	1.38(2)
N2	C26	1.471(9)	C23	C24	1.38(1)
C1	C2	1.36(1)	C26	C27	1.52(1)
C1	C6	1.40(1)	C26	C28	1.51(1)
C2	C3	1.37(1)	C26	C29	1.52(2)
C3	C4	1.40(1)	C30	C31	1.389(8)
C4	C5	1.34(1)	C30	C32	1.48(1)
C5	C6	1.40(1)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Bond Distances in Angstroms

BOND DISTANCES (Continued)

Atom 1 =====	Atom 2 =====	Distance =====	Atom 1 =====	Atom 2 =====	Distance =====
C2	H2	1.02(8)	C21	H21	0.81(8)
C3	H3	0.90(9)	C22	H22	0.8(1)
C4	H4	0.94(8)	C23	H23	0.92(8)
C5	H5	1.04(9)	C24	H24	1.07(8)
C6	H6	0.87(9)	C27	H271	0.98(8)
C8	H8	1.01(8)	C27	H272	1.03(9)
C9	H9	1.0(1)	C28	H281	0.91(9)
C10	H10	1.16(9)	C28	H282	1.09(9)
C11	H11	0.90(9)	C28	H283	0.78(8)
C12	H12	0.9(1)	C29	H291	0.75(9)
C14	H14	0.9(1)	C29	H292	0.88(8)
C15	H15	1.00(8)	C29	H293	0.81(9)
C16	H16	0.99(9)	C32	H321	0.77(8)
C17	H17	1.0(1)	C32	H322	0.89(8)
C18	H18	1.07(8)	C32	H323	0.7(1)
C20	H20	0.83(8)	C33	H331	0.61(9)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Bond Distances in Angstroms

BOND ANGLES FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$

Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====	Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====
P1	Rh	P2	167.24(6)	F3	P3	F4	179.1(4)
P1	Rh	N1	85.5(2)	F3	P3	F5	90.1(3)
P1	Rh	C25	92.4(2)	F3	P3	F6	88.1(3)
P2	Rh	N1	84.6(2)	F4	P3	F5	89.8(3)
P2	Rh	C25	98.0(2)	F4	P3	F6	91.0(4)
N1	Rh	C25	176.3(2)	F5	P3	F6	90.5(3)
Rh	P1	C13	121.0(4)	Rh	N1	C30	140.7(4)
Rh	P1	C19	107.5(3)	C25	N2	C26	175.3(8)
Rh	P1	C33	113.5(3)	P2	C1	C2	118.4(5)
C13	P1	C19	106.0(4)	P2	C1	C6	122.0(6)
C13	P1	C33	102.9(3)	C2	C1	C6	119.6(6)
C19	P1	C33	104.5(3)	C1	C2	C3	121.2(7)
Rh	P2	C1	108.2(3)	C2	C3	C4	118.5(8)
Rh	P2	C7	125.9(3)	C3	C4	C5	121.5(8)
C1	P2	C7	101.0(3)	C4	C5	C6	120.1(8)
F1	P3	F2	92.0(4)	C1	C6	C5	118.9(8)
F1	P3	F3	90.4(3)	P2	C7	C8	123.0(6)
F1	P3	F4	89.7(3)	P2	C7	C12	116.5(9)
F1	P3	F5	179.1(4)	C8	C7	C12	120.5(8)
F1	P3	F6	88.8(3)	C7	C8	C9	120.(1)
F2	P3	F3	91.7(4)	C8	C9	C10	120.(1)
F2	P3	F4	89.2(4)	C9	C10	C11	120.(1)
F2	P3	F5	88.7(3)	C10	C11	C12	121.(1)
F2	P3	F6	179.2(4)	C7	C12	C11	118.(1)

BOND ANGLES (Continued)

Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====	Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====
P1	C13	C14	120.6(8)	C21	C22	C23	121(1)
P1	C13	C18	120.6(7)	C22	C23	C24	119.1(9)
C14	C13	C18	118.5(8)	C19	C24	C23	119.7(8)
C13	C14	C15	122.(1)	Rh	C25	N2	176.1(6)
C14	C15	C16	119.(1)	N2	C26	C27	107.1(7)
C15	C16	C17	122.(1)	N2	C26	C28	107.8(7)
C16	C17	C18	118.(1)	N2	C26	C29	105.9(7)
C13	C18	C17	121.(1)	C27	C26	C28	110.8(9)
P1	C19	C20	125.5(5)	C27	C26	C29	112.1(8)
P1	C19	C24	115.7(6)	C28	C26	C29	112.7(9)
C20	C19	C24	118.7(8)	N1	C30	C31	107.7(6)
C19	C20	C21	122.6(8)	N1	C30	C32	122.2(6)
C20	C21	C22	118(1)	C31	C30	C32	130.0(7)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Bond Angles in Degrees

BOND ANGLES (Continued)

Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====	Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====
C1	C2	H2	121.(5)	C15	C16	H16	126.(5)
C3	C2	H2	118.(5)	C17	C16	H16	112.(5)
C2	C3	H3	111.(6)	C16	C17	H17	127.(6)
C4	C3	H3	131.(5)	C18	C17	H17	112.(6)
C3	C4	H4	117.(5)	C13	C18	H18	119.(5)
C5	C4	H4	122.(5)	C17	C18	H18	120.(5)
C4	C5	H5	122.(5)	C19	C20	H20	128.(6)
C6	C5	H5	117.(5)	C21	C20	H20	110.(6)
C1	C6	H6	127.(6)	C20	C21	H21	107.(7)
C5	C6	H6	114.(6)	C22	C21	H21	130.(7)
C7	C8	H8	119.(6)	C21	C22	H22	106.(8)
C9	C8	H8	121.(6)	C23	C22	H22	129.(8)
C8	C9	H9	114.(6)	C22	C23	H23	133.(5)
C10	C9	H9	123.(5)	C24	C23	H23	108.(5)
C9	C10	H10	109.(5)	C19	C24	H24	115.(4)
C11	C10	H10	131.(4)	C23	C24	H24	125.(4)
C10	C11	H11	111.(6)	C26	C27	H271	108.(5)
C12	C11	H11	127.(7)	C26	C27	H272	110.(5)
C7	C12	H12	127.(6)	H271	C27	H272	101.(7)
C11	C12	H12	115.(6)	C26	C28	H281	82.(7)
C13	C14	H14	121.(7)	C26	C28	H282	119.(4)
C15	C14	H14	117.(7)	C26	C28	H283	104.(7)
C14	C15	H15	125.(6)	H281	C28	H282	148.(8)
C16	C15	H15	116.(6)	H281	C28	H283	93.(9)

BOND ANGLES (Continued)

Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====	Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====
H282	C28	H283	104.(8)	C30	C32	H321	123.(9)
C26	C29	H291	108.(8)	C30	C32	H322	114.(6)
C26	C29	H292	109.(7)	C30	C32	H323	110.(9)
C26	C29	H293	106.(8)	H321	C32	H322	105.(9)
H291	C29	H292	100.(9)	H321	C32	H323	85.(28)
H291	C29	H293	123.(12)	H322	C32	H323	116.(12)
H292	C29	H293	110.(10)	P1	C33	H331	109.(10)

 Numbers in parentheses are estimated standard deviations in
 the least significant digits.

Bond Angles in Degrees

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD
DEVIATIONS FOR $[\text{Rh}_2(\mu\text{-dppm})_2(\text{t-BuNC})_2(\mu\text{-35MPz})](\text{PF}_6)_2$

Atom ----	x -	y -	z -	B(Å ²) -----
Rh	0.75003(2)	0.18728(2)	0.13783(1)	2.41(1)
P1	0.74419(7)	0.21874(7)	0.20936(6)	2.84(4)
P2	0.73324(7)	0.14853(7)	0.06723(7)	2.77(4)
P3	0.17198(9)	0.43679(9)	0.07337(7)	4.85(5)
F1	0.2394(2)	0.4268(2)	0.0909(2)	8.4(1)
F2	0.1439(3)	0.4291(3)	0.1206(2)	10.0(2)
F3	0.1658(3)	0.3665(2)	0.0640(2)	9.6(2)
F4	0.1785(2)	0.5079(2)	0.0820(2)	8.9(2)
F5	0.1051(2)	0.4475(2)	0.0554(2)	7.3(1)
F6	0.1993(2)	0.4445(3)	0.0256(2)	8.2(1)
N1	0.6612(2)	0.2201(2)	0.1324(2)	2.3(1)
N2	0.8842(2)	0.1476(2)	0.1505(2)	3.6(1)
C1	0.6747(3)	0.0889(3)	0.0706(2)	2.7(2)
C2	0.6845(3)	0.0406(3)	0.0981(3)	3.9(2)
C3	0.6418(3)	-0.0053(3)	0.1026(2)	4.6(2)
C4	0.5886(3)	-0.0027(3)	0.0774(3)	5.0(2)
C5	0.5779(3)	0.0441(3)	0.0501(3)	4.7(2)
C6	0.6215(3)	0.0905(3)	0.0451(2)	3.7(2)
C7	0.7909(3)	0.1107(3)	0.0325(2)	3.4(2)
C8	0.7915(4)	0.1161(3)	-0.0124(3)	4.6(2)
C9	0.8373(4)	0.0864(4)	-0.0366(3)	6.4(2)
C10	0.8786(4)	0.0492(4)	-0.0162(3)	6.9(2)
C11	0.8777(3)	0.0435(4)	0.0285(3)	7.0(2)

POSITIONAL PARAMETERS (Continued)

Atom ----	x -	y -	z -	B(Å ²) -----
C12	0.8337(3)	0.0736(3)	0.0538(3)	4.5(2)
C13	0.8124(3)	0.2321(3)	0.2410(2)	3.3(2)
C14	0.8626(3)	0.2595(3)	0.2225(2)	4.2(2)
C15	0.9131(3)	0.2755(3)	0.2470(3)	6.2(2)
C16	0.9130(4)	0.2640(4)	0.2897(3)	7.7(2)
C17	0.8634(5)	0.2362(4)	0.3103(3)	7.4(3)
C18	0.8132(4)	0.2206(4)	0.2851(3)	5.6(2)
C19	0.7007(3)	0.1613(3)	0.2390(2)	3.3(2)
C20	0.6500(3)	0.1722(3)	0.2631(3)	5.4(2)
C21	0.6170(4)	0.1261(4)	0.2828(3)	7.5(3)
C22	0.6358(5)	0.0669(4)	0.2767(4)	9.0(3)
C23	0.6888(4)	0.0535(3)	0.2541(3)	8.4(3)
C24	0.7207(3)	0.1005(3)	0.2340(3)	5.3(2)
C25	0.8342(3)	0.1619(3)	0.1442(2)	2.9(2)
C26	0.9463(3)	0.1261(3)	0.1614(3)	4.3(2)
C27	0.9619(3)	0.0752(3)	0.1295(3)	5.8(2)
C28	0.9897(3)	0.1797(4)	0.1561(3)	7.2(3)
C29	0.9428(4)	0.1031(4)	0.2082(3)	7.0(3)
C30	0.6027(3)	0.2018(3)	0.1376(2)	3.4(2)
C31	0.5649(4)	0.250	0.125	4.5(3)
C32	0.5867(3)	0.1406(3)	0.1550(3)	5.6(2)
C33	0.7003(3)	0.2906(3)	0.2169(2)	3.4(2)

 Anisotropically refined atoms are given in the form of the
 isotropic equivalent displacement parameter defined as:

$$(4/3) * [a^2 * \beta(1,1) + b^2 * \beta(2,2) + c^2 * \beta(3,3) + ab(\cos \gamma) * \beta(1,2) + ac(\cos \beta) * \beta(1,3) + bc(\cos \alpha) * \beta(2,3)]$$

POSITIONAL PARAMETERS (Continued)

Atom ----	x -	y -	z -	B(Å ²) -----
H2	0.723(3)	0.039(3)	0.117(2)	4.0*
H3	0.653(3)	-0.032(3)	0.124(2)	4.0*
H4	0.560(3)	-0.035(3)	0.081(2)	4.0*
H5	0.541(3)	0.044(3)	0.028(2)	4.0*
H6	0.612(3)	0.118(3)	0.026(2)	4.0*
H8	0.756(3)	0.137(3)	-0.027(2)	4.0*
H9	0.829(3)	0.084(3)	-0.068(2)	4.0*
H10	0.912(3)	0.030(3)	-0.042(2)	4.0*
H11	0.911(3)	0.023(3)	0.038(2)	4.0*
H12	0.837(3)	0.068(3)	0.084(2)	4.0*
H14	0.865(3)	0.265(3)	0.194(2)	4.0*
H15	0.949(3)	0.300(3)	0.236(2)	4.0*
H16	0.948(3)	0.271(3)	0.310(2)	4.0*
H17	0.854(3)	0.236(3)	0.341(2)	4.0*
H18	0.774(3)	0.199(3)	0.300(2)	4.0*
H20	0.633(3)	0.206(3)	0.268(2)	4.0*
H21	0.583(3)	0.140(3)	0.288(2)	4.0*

POSITIONAL PARAMETERS (Continued)

Atom -----	x -	y -	z -	B(A ²) -----
H22	0.618(3)	0.048(3)	0.293(2)	4.0*
H23	0.708(3)	0.017(3)	0.247(2)	4.0*
H24	0.763(3)	0.095(3)	0.217(2)	4.0*
H31	0.479(4)	0.750	0.125	4.0*
H271	1.004(3)	0.063(3)	0.135(2)	4.0*
H272	0.965(3)	0.093(3)	0.098(2)	4.0*
H273	0.069(3)	0.541(3)	0.113(2)	4.0*
H281	0.987(3)	0.180(3)	0.186(2)	4.0*
H282	0.989(3)	0.206(3)	0.126(2)	4.0*
H283	1.022(3)	0.164(3)	0.156(2)	4.0*
H291	0.974(3)	0.089(3)	0.214(2)	4.0*
H292	0.920(3)	0.070(3)	0.209(2)	4.0*
H293	0.927(3)	0.130(3)	0.222(2)	4.0*
H321	0.563(3)	0.119(3)	0.144(2)	4.0*
H322	0.619(3)	0.117(3)	0.160(2)	4.0*
H323	0.565(3)	0.143(3)	0.172(2)	4.0*
H331	0.674(3)	0.286(3)	0.211(2)	4.0*

Starred atoms were refined isotropically.

VITA

Louis Joseph Tortorelli, the youngest of four children, was born in Brooklyn, New York on May 5, 1959. He graduated from Northeast High School, Ft. Lauderdale, Florida in June 1977. After attending one year at Mercer University, Macon, Georgia and three years at the University of Mississippi, Oxford, he was awarded a B.A. in Chemistry, Psychology, and Zoology in May 1981. He then attended the University of South Florida, Tampa, for two years after which he accepted a Graduate Research-Teaching Assistantship from The University of Tennessee, Knoxville. He was awarded a Ph.D. in Chemistry from The University of Tennessee, Knoxville in June 1988.