

To the Graduate Council:

I am submitting herewith a dissertation written by Paul Daniel Enlow entitled "Structure, Properties, and Electrochemical Behavior of Some Binuclear Rhodium Complexes Containing Isocyanide, Carbon Monoxide, and Halide Ligands." 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.

Clifton Woods
Clifton Woods, Major Professor

We have read this dissertation
and recommend its acceptance:

M. J. Sepaniak
Daniel Fox
William E Bull

Accepted for the Council:

LeWinkler
The Graduate School

STRUCTURE, PROPERTIES, AND ELECTROCHEMICAL BEHAVIOR OF SOME
BINUCLEAR RHODIUM COMPLEXES CONTAINING ISOCYANIDE, CARBON
MONOXIDE, AND HALIDE LIGANDS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Paul Daniel Enlow

August 1984

ACKNOWLEDGMENTS

I wish to express my appreciation to the Department of Chemistry, The University of Tennessee, Knoxville, for financial aid in the form of graduate teaching and graduate teaching/research assistantships.

My special thanks goes to Dr. Clifton Woods, III for his generous support, guidance, humor, and patience during my career at UT. I also wish to thank Dr. J. Q. Chambers for his helpful comments. I am grateful to Dr. Gilbert Brown of the Oak Ridge National Laboratory for his fluorescence measurements and comments.

I wish to acknowledge the Dow Corporation and Research Corporation for financial aid in the form of research grants.

Special thanks also goes to Dr. Lew Keller of the Chemistry Division of the Oak Ridge National Laboratory for funds for the purchase of the photolysis equipment used in this research, and also for funds in the form of a graduate research stipend.

My gratitude is extended to Dave Abbott, Celeste Daffron, Charles Fraley, Stan Manning, Peter Tinsley, Betty Williams, and Don Womack for not only aiding my research, but also for making my stay in Tennessee a better one.

ABSTRACT

Binuclear rhodium complexes containing isocyanide, carbon monoxide, halide, and the bridging ligands DPM, DAM, and DADPM (DPM = bis(diphenylphosphino)methane; DAM = bis(diphenylarsino)methane; DADPM = (diphenylarsino)(diphenylphosphino)methane) have been investigated. Some aspects of the photolytic and the electrochemical behavior of $[\text{Rh}_2(\text{RNC})_4(\text{DPM})_2]\text{X}_2$ ($\text{R} = \text{CH}_3$, $i\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, $t\text{-C}_4\text{H}_9$; $\text{X} = \text{PF}_6^-$; BF_4^-) in coordinating and non-coordinating media are discussed. These compounds are capable of generating dihydrogen in aqueous acetone and are rapidly oxidized in solution in the presence of light at 520 nm. Electrochemical oxidation in the presence of coordinating species produces $[\text{Rh}_2(\text{RNC})_4\text{Y}_2(\text{DPM})_2]\text{X}_2$ ($\text{Y} = \text{CN}^-$, SCN^- , I^- , substituted pyridine). The structure and electrochemistry of $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DADPM})_2$ is also investigated. The reactivities and stabilities of $\text{Rh}_2(\text{CO})_2(\text{DADPM})_2$ have also been investigated. The reactivities and stabilities of $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DADPM})_2$ and its derivatives have been compared with the analogous DPM and DAM compounds. The new DADPM complexes are characterized by infrared, ultraviolet-visible, and ^{31}P and ^{13}C NMR techniques.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION.	1
A. General	1
B. Binuclear Rhodium Complexes Containing Halogens and Carbon Monoxide	7
C. Tetrakis(isocyanide) Rhodium(I) Complexes and Hydrogen Generation	12
D. Purpose of Work	14
II. EXPERIMENTAL.	16
A. Chemicals	16
1. Reagents	16
2. Gases	21
3. Solvents.	21
B. Instrumentation	23
1. Spectroscopy	23
2. Electrochemistry	24
3. Photolysis	26
C. Production and Detection of Hydrogen from $[(CH_3NC)_4Rh_2(DPM)_2](PF_6)_2$	26
1. Blank runs.	26
2. Production of Hydrogen from $[Rh_2(CH_3NC)_4$ $(DPM)_2](PF_6)_2$, <u>22</u>	28
D. Elemental Analysis.	28
E. Synthesis	29
1. Diphenylarsino(diphenylphosphino)methane $(C_6H_5)_2AsCH_2(C_6H_5)_2$, DADPM	29
2. Dicarbonyldichlorobis[μ -{[(diphenylarsino)methyl]- diphenylphosphine-As:P}]dirhodium(I), $Rh_2(CO)_2Cl_2(DADPM)$, <u>29</u>	30
3. ^{13}C analogue of <u>29</u> , $Rh_2(^{13}CO)_2Cl_2(DADPM)_2$	30
4. Dicarbonyldichlorobis[μ -methylenebis[diphenyl- phosphine]-P;P']dirhodium(I), $Rh_2(CO)_2Cl_2$ - $(DPM)_2$, <u>1</u>	31
5. Dicarbonyldichlorobis[μ -methylenebis- [diphenylarsine]-As:As']dirhodium(I), $Rh_2(CO)_2Cl_2(DAM)_2$, <u>2</u>	31
6. Tetrakis(2-isocyano-2-methylpropane)bis- [μ -methylenebis[diphenylphosphine]-P;P']- dirhodium(I) bis[hexafluorophosphate], $[Rh(t-C_4H_9NC)_4(DPM)_2](PF_6)_2$, <u>23</u>	31
7. Tetrakis(2-isocyanopropane)bis[μ -methylene- bis[diphenylphosphine]-P;P']dirhodium(I) bis[hexafluorophosphate], $[Rh_2(i-C_3H_7NC)_4(DPM)_2]$ - $(PF_6)_2$, <u>25</u>	32

8. Tetrakis(2-isocyanopropane)bis[μ -methylene-bis[diphenylphosphine]-P:P']dirhodium(I) bis[tetrafluoroborate], $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{BF}_4)_2$, 26 33
9. Tetrakis(2-isocyanobutane)bis[μ -methylene bis[diphenylphosphine]-P:P']dirhodium(I) bis[hexafluorophosphate], $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 27 33
10. μ -Carbonyldicarbonyl- μ -chlorobis[μ -{[(diphenylarsino)methyl]diphenylphosphine-As:P}]dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-Cl})-(\text{DADPM})_2](\text{PF}_6)_2$, 32 33
11. Dicarbonyl- μ -chlorobis[μ -{[(diphenylarsino)methyl]diphenylphosphine-As:P}]dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DADPM})_2](\text{PF}_6)_2$, 35 34
12. Bromo- μ -carbonyldicarbonylbis[μ -{[(diphenylarsino)methyl]diphenylphosphine-As:P}]dirhodium(I) bromide, $[\text{Rh}_2\text{Br}(\mu\text{-CO})(\text{CO})_2(\text{DADPM})_2]\text{Br}$, 38 34
13. Dicarbonylchloro(2-isocyano-2-methylpropane)-bis[μ -{[(diphenylarsino)methyl]diphenylphosphine-As:P}]dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\text{CO})_2\text{Cl}(\text{t-C}_4\text{H}_9\text{NC})(\text{DADPM})_2](\text{PF}_6)_2$, 44 35
14. Carbonylchlorobis(2-isocyano-2-methylpropane)-bis[μ -{[(diphenylarsino)methyl]diphenylphosphine-As:P}]dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\text{CO})\text{Cl}(\text{t-C}_4\text{H}_9\text{NC})_2(\text{DADPM})_2](\text{PF}_6)_2$, 45 35
15. Tetrakis(isocyanocyclohexane)bis[μ -{[(diphenylarsino)methyl]diphenylphosphine-As:P}]dirhodium(I) bis(hexafluorophosphate), $[\text{Rh}_2(\text{c-C}_6\text{H}_{11}\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$, 47 36
16. Tetrakis(2-isocyanopropane)bis[μ -{[(diphenylarsino)methyl]diphenylphosphine-As:P}]dirhodium(I) bis(hexafluorophosphate), $\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$, 46 37
17. Tetrakis(2-isocyano-2-methylpropane)bis[μ -{[(diphenylarsino)methyl]diphenylphosphine-As:P}]dirhodium(I) bis(hexafluorophosphate), $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$, 48 37
18. Dicarbonyl- μ -chlorodichlorobis[μ -{[(diphenylarsino)methyl]diphenylphosphine-As:P}]dirhodium(I) tetrafluoroborate, dichloromethane adduct, $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}_2(\text{DADPM})_2](\text{BF}_4) \cdot 1/2 \text{CH}_2\text{Cl}_2$, 54 38

CHAPTER	PAGE
19. Tetrakis(2-isocyanopropane)dithiocyanato- bis[μ -methylenebis[diphenylphosphine]-P:P']- dirhodium(II) bis(tetrafluoroborate), [Rh ₂ (η -C ₃ H ₇ NC) ₄ (SNC) ₂ (DPM) ₂](BF ₄) ₂ , 59	38
20. Tetrakis(2-isocyanopropane)dicyanobis[μ -methylene- bis[diphenylphosphine]-P:P']dirhodium(II) bis- (tetrafluoroborate), [Rh ₂ (η -C ₃ H ₇ NC) ₄ (CN) ₂ - (DPM) ₂](BF ₄) ₂ , 60	39
21. Attempted syntheses of dichloro rhodium(II) complexes of the type [Rh ₂ (RNC) ₄ Cl ₂ (DPM) ₂], X ₂ , X = PF ₆ ⁻ , BF ₄ ⁻	40
F. Compound Identification	42
III. PHOTOLYSIS AND HYDROGEN GENERATION INVOLVING BINUCLEAR RHODIUM TETRAKISISOCYANIDE COMPLEXES.	46
IV. STRUCTURE AND PROPERTIES OF BINUCLEAR RHODIUM COMPLEXES CONTAINING HALIDE AND CARBON MONOXIDE LIGANDS	57
V. ELECTROCHEMISTRY OF BINUCLEAR RHODIUM COMPLEXES CONTAINING ISOCYANIDE AND CARBON MONOXIDE LIGANDS	77
A. Electrochemical Behavior of Binuclear Rhodium Complexes Containing Chloride and Carbon Monoxide Ligands	78
B. Electrochemical Behavior of Tetrakisisocyanide Complexes in Dichloromethane.	82
C. Electrochemical Behavior of Tetrakisisocynamide Complexes in Acetonitrile	98
D. Electrochemical Investigation of the Coordination of Substituted Pyridines to Binuclear Rhodium(II) Tetrakisisocyanide Complexes.	103
VI. CONCLUSIONS	124
LIST OF REFERENCES	126
VITA	133

LIST OF TABLES

TABLE	PAGE
I. Compound Identification	43
II. Change of Absorbance with Time for $4.4 \times 10^{-5} \text{ M}$ $[\text{Rh}_2(\underline{\text{t}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in Oxygenated CH_2Cl_2 . . .	54
III. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectral Data for Selected Compounds Containing DADPM.	59
IV. IR and UV-Vis Spectral Data for Selected Compounds Containing DADPM	76
V. Voltammetric Data for $[(\underline{\text{i}}\text{-C}_3\text{H}_7\text{NC})_4\text{Rh}_2(\text{DPM})_2](\text{PF}_6)_2$. .	87
VI. Aqueous Base Strengths for Selected Substituted Pyridines	104
VII. Relationship between ΔE for $[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2]-$ $(\text{PF}_6)_2$ and the $\text{p}K_{\text{b}}$ of the Coordinating Pyridine	120

LIST OF FIGURES

FIGURE	PAGE
1. Simple qualitative orbital energy diagram for association of $\text{Rh}(\text{RNC})_4^+$ in solution.	3
2. Experimental set-up for detecting hydrogen evolution from binuclear rhodium complexes.	27
3. UV-Vis absorption spectra of $5 \times 10^{-5} \text{ M}$ $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, <u>23</u> , in CH_3Cl_2	49
4. UV-Vis difference spectrum between curves 1 and 2 of Figure 3.	51
5. UV-Vis spectra of $4.5 \times 10^{-5} \text{ M}$ $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in oxygenated CH_2Cl_2	52
6. UV-Vis spectrum of $4.3 \times 10^{-5} \text{ M}$ $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2	53
7. IR spectra (KBr) of $\text{Rh}_2(\text{CO})_2\text{Cl}_2\text{L}_2$	61
8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Rh}_2(^{13}\text{CO})_2(\text{DADPM})_2$	63
9. IR spectra (Nujol) of $[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2\text{Cl}(\text{DADPM})_2]\text{PF}_6$	67
10. IR spectrum (Nujol) of $\text{Rh}_2\text{Br}_2(\mu\text{-CO})(\text{CO})_2(\text{DADPM})_2$	69
11. Three possible isomers for $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})-(\text{DPM})_2]\text{BF}_4 \cdot 1/2 \text{ CH}_2\text{Cl}_2$	81
12. Cyclic voltammograms of (a) 10^{-3} M $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DADPM})_2$ in CH_3CN , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$, and $2 \times 10^{-3} \text{ M}$ $(\text{C}_4\text{H}_9)_4\text{NCl}$ and (b) the same system as Figure 12a oxidized at +0.65 V.	83

FIGURE	PAGE
13. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$	85
14. Plot of the anodic peak current (i_{pa}) vs. $v^{1/2}$ for the quasi-reversible couple in Figure 13 (page 85).	88
15. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M $(\text{C}_4\text{H}_9)_4\text{NCl}$	90
16. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M $(\text{C}_4\text{H}_9)_4\text{NCl}$ after oxidation at +0.75 V	91
17. Cyclic voltammogram of 2.5×10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{N}(\text{PF}_6)_2$, and 10^{-2} M $(\text{C}_4\text{H}_9)_4\text{NCl}$ after oxidation at +0.75 V.	93
18. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M $[(\text{C}_5\text{H}_4\text{N})\text{C}_4\text{H}_9]\text{Cl}$ (temperature = $20.4 \pm 0.2^\circ\text{C}$).	94
19. Cyclic voltammograms of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M $[(\text{C}_5\text{H}_4\text{N})\text{C}_4\text{H}_9]\text{Cl}$ at various temperatures: (a) $6.4 \pm 0.2^\circ\text{C}$; (b) $-10.7 \pm 0.02^\circ\text{C}$; and (c) $-39.7 \pm 0.2^\circ\text{C}$	95

20. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_3CN and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ 99
21. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_3CN and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ after oxidation at +1.3 V. 101
22. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ 106
23. Cyclic voltammograms of 10^{-3} M $[\text{Rh}(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 ; 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$; and (a) 1×10^{-3} M 3-cyanopyridine; (b) 2×10^{-3} M 3-cyanopyridine; and (c) 4×10^{-3} M 3-cyanopyridine 108
24. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4\text{Rh}_2(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M 4-cyanopyridine. 110
25. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M 4-benzoylpyridine. 111
26. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ and 4×10^{-3} M pyridine 112
27. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M 4-ethylpyridine. 113

FIGURE

PAGE

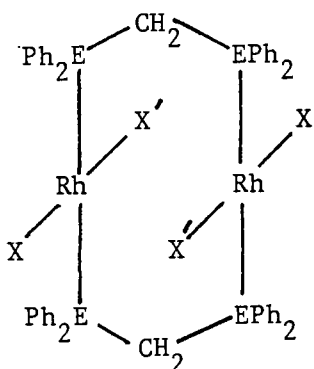
28. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M 3,4-dimethylpyridine 114
29. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M 4-(dimethylamino)pyridine 115
30. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M pyridine 117
31. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $\text{C}_4\text{H}_9\text{NPF}_6$, and 4×10^{-3} M pyridine 118
32. Plot of ΔE vs. $\text{p}K_b$ for $[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in the presence of substituted pyridines 121
33. Simplified molecular orbital energy diagram for the coordination of substituted pyridines to binuclear rhodium complexes. 122

CHAPTER I

INTRODUCTION

A. General

In recent years great interest has been shown in binuclear rhodium complexes containing bridging phosphine and arsine ligands. Much of this interest has been generated by investigations of the structure and properties of binuclear Rh(I) complexes such as the dihalo dicarbonyl species¹⁻⁴ trans-[Rh(CO)Cl(DPM)]₂, 1, and trans-Rh(CO)Cl(DAM)]₂, 2, and the tetrakisocyanide compounds^{2,5,6} [Rh(RNC)₂(DPM)]₂²⁺, 3, and [Rh(RNC)₂(DAM)]₂²⁺, 4 (DPM=Ph₂PCH₂PPh₂, DAM=Ph₂AsCH₂AsPh₂). The possibility that dimeric Rh(I) compounds can



- 1; E = P, X = CO, X' = Cl
- 2; E = AS, X = CO, X' = Cl
- 3; E = P, X = X' = RNC
- 4; E = AS, X = X' = RNC

be readily made from monomers to give complexes similar to 1-4 was first discovered during investigations of square planar Rh(RNC)₄⁺ species (R = CH₃, C₂H₅, etc.). It appears that oligomerization of these compounds in solution readily occurs via weak Rh-Rh bonding due

to rhodium d_{z^2} orbital interaction.⁶ In fact, although solid state self-association of square planar systems has long been known, oligomerization of d^8 systems in solution was not common until Rh(I) tetrakis(isocyanides) were investigated.²

The first evidence for association of Rh(I) monomers in solution was reported in 1956 when Malatesta and Vallarino⁷ noted that violet solutions were produced upon addition of colorless aryl isocyanides to red $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. While a satisfactory explanation of the color change eluded those authors, it is now known that the deep blue-violet color characteristic of binuclear rhodium isocyanides is due to the splitting of the electronic energy levels caused by the interaction of the metal p_z , and d_{z^2} orbitals in the dimer.^{6,8} This energy level splitting and concomitant reduction in electronic transition energy is illustrated by the simple orbital energy diagram shown in Figure 1. In a dilute solution of $\text{Rh}(\text{RNC})_4^{2+}$ no appreciable association occurs, and the lowest energy electronic transition is a metal-to-ligand charge transfer transition $1a_{1g}(d_{z^2}) \rightarrow 1a_{2u}(\pi^*)$, that occurs at ca. 380 nm.⁹ In a solution that is concentrated enough for dimeric association to occur, the interaction between the metal d_{z^2} , p_z , and ligand π^* orbitals gives the energy levels shown in Figure 1 for $[\text{L}_4\text{Rh}-\text{RhL}_4]^{2+}$. The lowest energy transition is a metal centered^{6,8,10} $1a_{2u}(d_{z^2}) \rightarrow 2a_{1g}(p_z)$ transition that occurs at 490-570 nm depending upon the bulk of R.¹¹ Smaller R groups allow a closer approach of the rhodium atoms than larger R groups so that the rhodium-rhodium

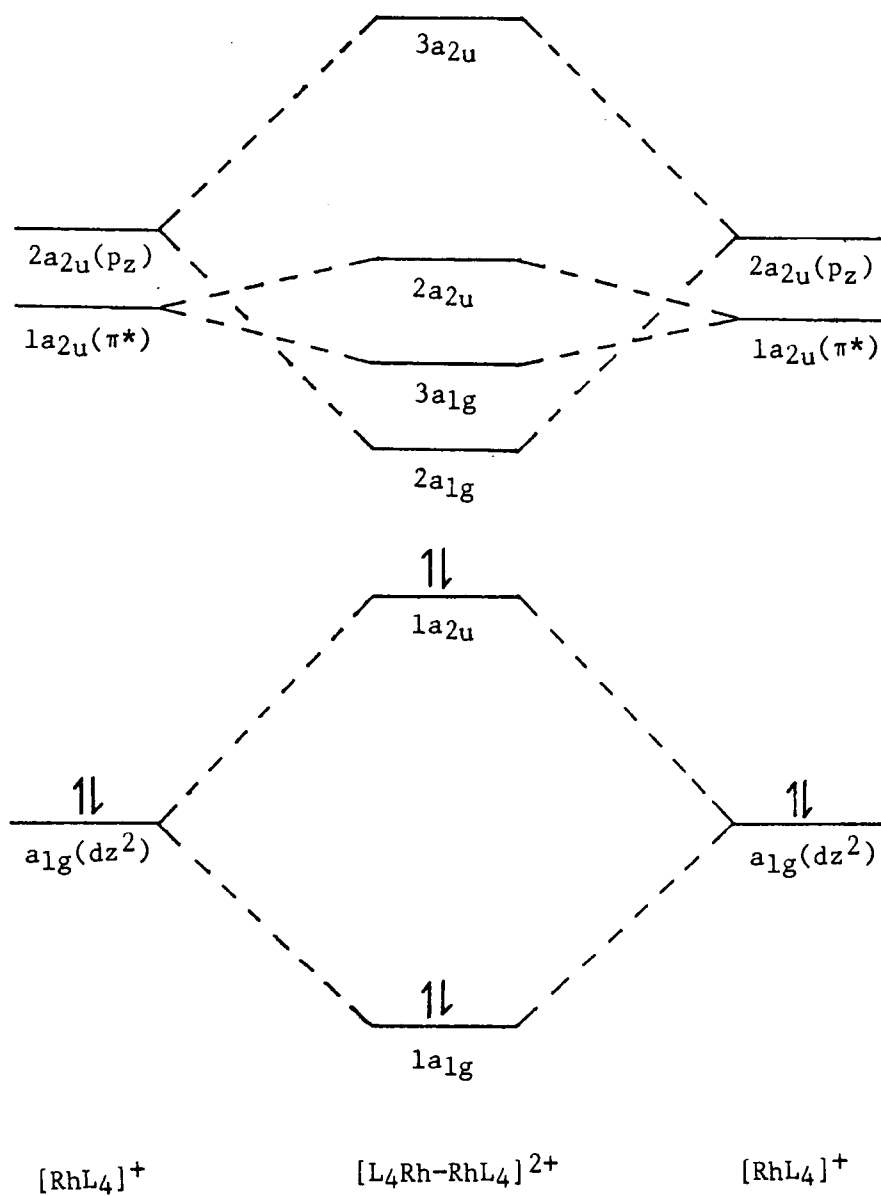


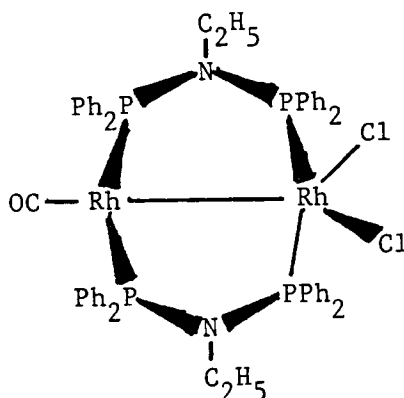
Figure 1. Simple qualitative orbital energy diagram for association of $\text{Rh}(\text{RNC})_4^+$ in solution.

interaction responsible for shifting the orbital energies in Figure 1 is stronger when the metals are coordinated to smaller ligands. Therefore, the energy of the metal centered electronic transition decreases as the bulk of R decreases. If the concentration of $\text{Rh}(\text{RNC})_4^+$ is increased beyond the region where the dimer is seen, trimeric¹¹⁻¹³ and even tetrameric¹¹ species exist that exhibit absorptions at ca. 610-730 and ca. 960 nm, respectively.

The dependence of the color changes of $\text{Rh}(\text{RNC})_4^+$ solutions upon direct metal-metal interactions has been corroborated by Balch and Olmstead,¹⁴ who have shown that appreciable spectral changes with concentration for $\text{Rh}(\text{RNC})_4^+$ do not occur when R is bulky, e.g., t-butyl. Since metal-metal interaction is only allowed for square planar Rh(I) complexes that are composed of nonbulky ligands, Rh(I) monomers with triphenylphosphine or arsine ligands have not been known to dimerize in solution.² Similarly, DPM- and DAM-bridged dimers, such as 1-4, show little or no tendency to oligomerize with increasing concentration; this is most likely due to the steric demands of the bulky phenyl groups on the DPM and DAM.² However, oligomerization of binuclear rhodium complexes containing bridging ligands can occur as long as such ligands allow intermolecular rhodium interactions. This is the case for the oligomerization of $[\text{Rh}_2(\text{bridge})_4]^{2+}$, 5, (bridge = 1, 4-diisocyanopropane).¹⁵⁻¹⁷

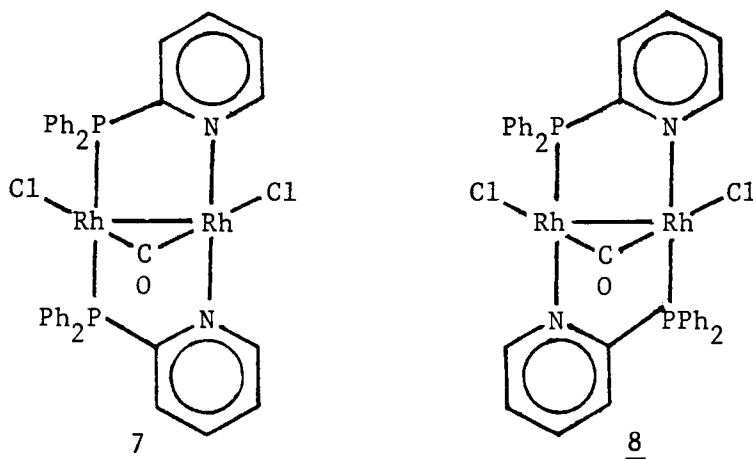
In addition to the diisocyanopropane and the DPM and DAM species mentioned previously, several other ligands capable of bridging square planar rhodium systems have been reported. Balch and Tulyathan¹⁸ have

investigated compounds analogous to 1 using $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 3, 4$) as the bridging ligand. The resulting complexes do not show any shifts in their electronic bands due to a close approach of the metal centers since the rhodium-rhodium distance is large relative to their DPM and DAM analogues. It should be noted that in the dimer containing $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ as the bridging ligand, a rhodium-rhodium interaction would be expected.¹⁸ However, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ tends to complex as a bidentate ligand, resulting in a chelated rhodium monomer.¹⁹ Similar chelation has also been seen for $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ and $\text{Ph}_2\text{AsCH}=\text{CHAsPh}_2$.² A binuclear rhodium carbonyldichloro complex bridged by the ditertiary phosphite $(\text{PhO})_2\text{PN}(\text{C}_2\text{H}_5\text{P})(\text{OPh})_2$, (etdp), has been reported by Haines *et al.*²⁰ The compound, $\text{Rh}_2(\text{CO})\text{Cl}_2(\text{etdp})_2$, 6, is a mixed valence $\text{Rh}(\text{O})$ - $\text{Rh}(\text{II})$ complex presumably with a direct rhodium-rhodium bond so that both metal atoms are 16 electron systems.

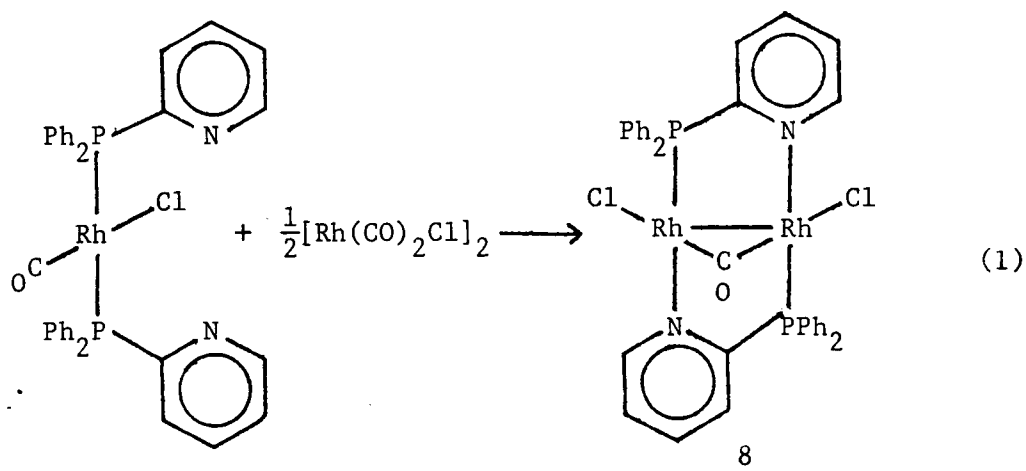


Haines has also reported that the etdp species can behave as a chelating ligand as well as a bridging ligand in Rh(I) dimers.²¹ Other bridging ligands that have been used in orienting square planar rhodium units in a face-to-face fashion so that a rhodium-rhodium interaction is seen include carboxylate^{18,22,23} ions, the diphenyltriazeno ion¹⁸ $[(\text{PhN})\text{N}(\text{NPh})]^-$, and various heterocyclic compounds containing two nitrogen donor sites^{24,25} such as 4,4'-bipyridine, pyrazine, 4-cyanopyridine, and pyrazole.

Investigations of binuclear rhodium complexes have generally been limited to systems with symmetrical bridging ligands such as DPM or DAM. Recently Balch and coworkers^{26,27} have introduced a binuclear rhodium complex bridged by unsymmetrical 2-(diphenylphosphino)pyridine, (Ph_2Ppy). Compounds of this type can conceivably exist either in a head-to-head or head-to-tail arrangement of the bridging ligands, as illustrated by compounds 7 and 8 respectively.²⁷ The actual structure has been shown by Balch via X-ray crystallography to be 8 the head-to-tail isomer. It is significant that 8 can be made either by stoichiometric addition



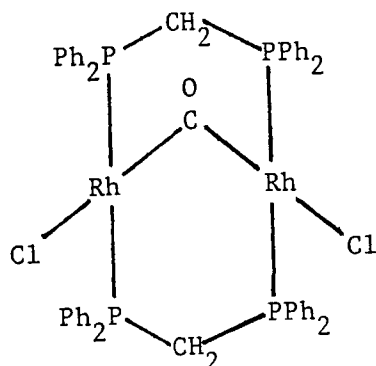
of the Ph_2Ppy to $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$, or by equation (1), in which $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$ is added to $\text{Rh}(\text{CO})\text{Cl}(\text{Ph}_2\text{Ppy})_2$. This second procedure does not produce the head-to-head complex 7 (p 6), but a rhodium-phosphorus bond breaks in the $\text{Rh}(\text{CO})\text{Cl}(\text{Ph}_2\text{Ppy})_2$ and the pyridine ligand rearranges to form 8 (p 6).^{26,27}



Another unsymmetrical ligand that will readily form binuclear rhodium complexes is $\text{Ph}_2\text{AsCH}_2\text{PPh}_2$ (DADPM).^{28,29} Rhodium complexes containing this ligand have recently been synthesized and studied²⁹ as a part of the work presented in this dissertation and will be discussed in more detail later.

B. Binuclear Rhodium Complexes Containing Halogens and Carbon Monoxide

A great deal of the current interest in compounds 1 (p 1) and 2 (p 1) is due to their ability to form "A-frame" complexes^{3,4,30-40} illustrated by $\text{Rh}_2(\mu\text{-CO})(\text{Cl}_2)(\text{DPM})_2$, 9.^{30,33} Complexes of this type

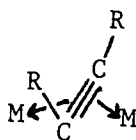
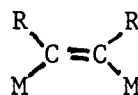


9

that contain an "active site"^{33,34} capable of accommodating small molecules are of particular interest. This is true in the case of coordination of acetylenes across the metal-metal distance^{38,41-45} because of the possible application of compounds of types 1 (p 1) and 9 as homogeneous catalysts.^{3,41,42} The use of binuclear complexes, metal clusters, and metal surfaces in the investigation of catalytic phenomena has increased recently, especially with respect to modes of bonding and reactivity of olefins and acetylenes.⁴⁶ Coordination of acetylenes to binuclear complexes usually occurs through oxidative-addition and results in a lengthening of the carbon-carbon bond, thus activating the acetylene toward reactions such as hydrogenation and oligomerization.^{41,46} The degree of activation of the olefinic or acetylenic bond is thought to be directly related to the change in the carbon-carbon bond distance.⁴⁶ For example, Cowie⁴¹ has reported that the triple bond in $\text{CH}_3\text{O}_2\text{CCCCO}_2\text{CH}_3$ (DMA) is

increased from 1.20 Å^{41,47} in the free molecule to 1.32 Å⁴¹ in the coordinated ligand. This indicates a reduction in the carbon-carbon bond order.

Several possible configurations exist for acetylenes coordinated to two metal centers,⁴⁶ but the most probable geometries are given as 10 and 11.^{41,43,44,46} Configuration 10 may be pictured as a dihapto bimetallic π complex where the carbon-carbon bond is perpendicular to

1011

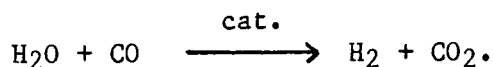
the metal-metal axis. Structure 11 is a σ -bonded cis-dimetalated complex in which the carbon and metal axes are parallel.

Differentiation between coordination modes 10 and 11 is important since Muetterties⁴⁶ maintains that the dihapto bonding system 10 will result in a greater degree of activation of the acetylene than will the cis-dimetalated configuration 11. This idea is supported by Dickson *et al.*⁴⁴ who have shown that the acetylenic bond in $\text{CF}_3\text{C}_2\text{CF}_3(\text{HFB})$ is much longer in the dihaptoacetylene complex $\text{Rh}_2(\text{Cp})_2(\mu\text{-CO})(\mu\text{-HFB})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), where the carbon-carbon distance of 1.36 Å is longer than it is in the cis-dimetalated acetylene complex,⁴³ $\text{Rh}_2(\text{Cp})_2(\text{CO})_2(\mu\text{-HFB})$, where the analogous distance is 1.27 Å.

Investigations of the interactions between acetylenes and binuclear rhodium complexes have shown that coordination of the acetylenes readily occurs. Cowie and Southern^{41,45} have coordinated DMA and HFB to 1 (p 1), 8 (p 6), and the bromo and iodo analogues of 9 (p 7) under mild conditions. X-ray crystallography⁴⁷ has shown that one of the resulting complexes, $\text{Rh}_2\text{Cl}_2(-\text{CO})(-\text{DMA})(\text{DPM})_2$, 12, is a cis-dimetallated olefin (c.f. 11 p 9) where the olefin lies approximately in a plane that contains the rhodium atoms and the bridging carbon monoxide and is perpendicular to the rhodium-phosphorus axes. Compound 9 (p 8) is the first characterized rhodium complex to contain a ketonic carbonyl (the term ketonic carbonyl is given to a carbonyl group bridging two metals that are not formally bonded to each other).^{41,45} Cowie and Dickson⁴² have produced the cis-dimetallated olefin complex $\text{Rh}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2$, 13, either by CO loss from 12 or by addition of DPM and HFB to $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$. These authors also showed that 13 reacts with CO to produce 12 with retention of the cis-dimetallated configuration. This is in contrast to results obtained by Dickson and coworkers⁴⁴ in which the cis-dimetallated $\text{Rh}_2(\text{Cp})_2\text{CO}_2(\mu\text{-HFB})$, 14, changes to the dihapto $\text{Rh}_2(\text{Cp})_2(\mu\text{-CO})(\mu\text{-HFB})$, 15, upon loss of CO. The production of 15 from 14 is reversible upon treatment of 15 with CO at 25°C and 1 atm.⁴⁸

Several A-frame rhodium complexes have demonstrated the ability to act as homogeneous catalysts in addition to simply coordinating to multiple-bonded systems. Some unspecified A-frame complexes of Mague

and DeVries³ have been reported to catalyze the hydrogenation of various olefins and acetylenes. Cowie⁴¹ reports that compound 9 (p 8) catalyzes the cyclotrimerization of DMA at room temperature as well as the hydrogenation of phenylacetylene and diphenylacetylene. The failure of 9 to catalyze the hydrogenation of DMA is reportedly due to the high electron withdrawing ability of DMA. Hydrogenation of coordinated acetylenes is favored by high electron density on the metal atoms resulting from low formal oxidation number and/or the presence of strong σ donor ligands,⁴⁶ but since the oxidation number of rhodium in 12 (p 10) is formally +3, oligomerization occurs rather than hydrogenation.⁴¹ Another catalytic system of note is the purple, highly reactive Rh(0) complex³⁸ $\text{Rh}_2(\text{CO})_2(\text{DPM})_2$, 16, which readily hydrogenates acetylene and phenylacetylene. Addition of CO, or CO and H^+ to 16 produces the tricarbonyl $\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\text{DPM})_2$, 17, or the hydride-bridged species $\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\text{DPM})_2]^+$, 18, respectively. Alkylnitrosoureas readily react with 17 to produce $\text{Rh}_2(\text{NCO})_2(\text{CO})_2(\text{DPM})_2$, 19, plus various products such as H_2 , CO, and CO_2 .⁴⁷ Compound 19 rearranges to form $[\text{Rh}_2(\mu\text{-NCO})(\text{CO})_2(\text{DPM})_2]^+$ which catalyzes the hydrogenation of ethylene at 60°C .³⁷ Complex 18 has been demonstrated to be an outstanding water gas shift catalyst:³⁸



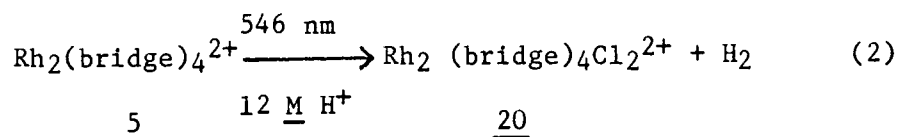
C. Tetrakis(isocyanide) Rhodium(I) Complexes and Hydrogen Generation

Although the primary interest in the tetrakis(isocyanide) binuclear rhodium complexes^{2,3,5,6} 3 (p 1) and 4 (p 1) has arisen due to general investigations of metal-metal interactions,^{2,5} these complexes are also of interest because of their electronic and structural similarity to 5 (p 4), which is capable of the photochemical generation of dihydrogen. While much work concerning H₂ production has been done by a variety of authors,⁴⁹⁻⁵³ the use of the binuclear rhodium complex 5 (p 4) in the photochemical generation of hydrogen has been extensively investigated by Gray and co-workers.^{16,49,53-56}

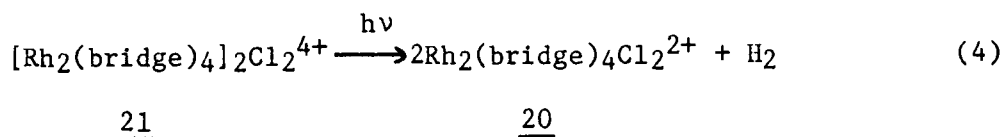
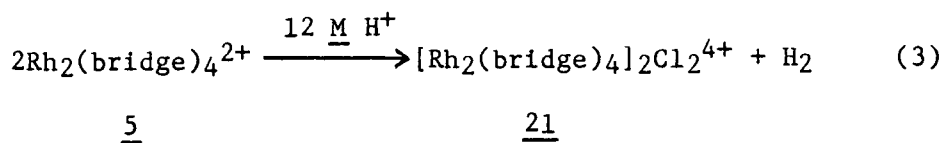
The use of solar energy for photolytic processes has obvious economic advantages over other energy sources. However, the vast majority of the energy in sunlight lies at long wavelengths, the near IR and yellow-red end of the visible regions of the spectrum. This precludes the use of many systems that are photosensitive to ultraviolet light. The importance of employing the visible solar spectrum in photochemical work is reflected in the maximum attainable efficiencies of solar energy storage systems based solely upon excitation of the photoactive species. At a wavelength of 400 nm the efficiency of such systems is estimated to be 0.04; at 600 nm the efficiency rises to 0.22.⁴⁹ Therefore, some binuclear rhodium(I) systems are candidates for use in the photolytic production of H₂ from H₂O or H⁺ since the lowest energy electronic transition is "proximity shifted" (Figure 1, page 3) into the visible regions of the

spectrum. This suggests that visible solar radiation can be used to possibly activate the compound toward hydrogen generation.

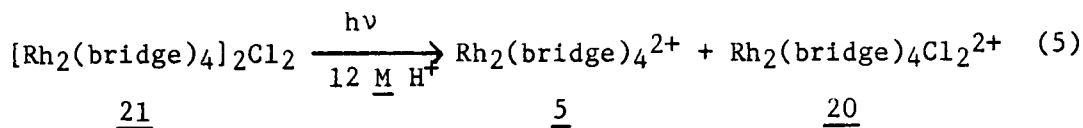
Dihydrogen production via 5 (p 4) was originally thought to be a relatively simple photochemical process involving transannular oxidative addition of Cl^- to 5 (p 4) in 12 M HCl with irradiation at 546 nm (Equation 2).^{53,54} The resulting Rh(II) complex 20 has been



characterized as being identical to the product resulting from direct oxidative addition of Cl_2 to 5.^{15,54} Reaction (2) was later found^{16,53,56} to be much more complex than simple oxidative addition to 5 with concomitant reduction of H^+ ; it is probable that (2) consists of an initial thermal reaction (3) that produces a photoactive tetranuclear Rh(1 1/2) species 21,^{53,55} followed by the photochemical process (4).⁵³ The latter reaction most likely involve the photolytic disproportionation of 21 into 5



and 20 (Equation 5) followed by the thermal reaction (3) with compound 5.



It actually appears that the thermal process (3) produces as much H₂ as does the photolytic process (4),^{55,56} resulting in an overall 1:1 stoichiometry for the hydrogen production as given by (2).

D. Purpose of Work

Although X-ray studies have shown 1 (p 1) and 2 (p 1) to be isostructural,^{1,4} the derivatives of 1 and 2 have been shown in many cases to be different in terms of structure, stability, and reactivities^{3,4,39} These differences are largely due to the different "bite" sizes of the bridging DPM and DAM ligands. Since DAM has the larger bite, derivatives of 2 tend to have a larger rhodium-rhodium separation than derivatives of 1,^{3,35,57} thus the structures and stabilities of the two types of complexes are affected differently, especially in cases where bridging by small species such as CO or halides is possible.³⁹

Due to the differences in the derivatives of 1 and 2, it is of interest to investigate analogous complexes of the ligand Ph₂AsCH₂PPh₂, DADPM. Since the bite of DADPM is expected to be between that of DPM and DAM, the binuclear complexes of DADPM should also have a metal-metal separation between that of the DPM and DAM

complexes. Therefore, it is of interest to compare the structure and stability of DADPM compounds with the corresponding DPM and DAM species, particularly in cases where the latter two systems differ.

Differences in reactivities of rhodium dimers due to different rhodium-rhodium separations, and the potential role that the rhodium-rhodium separation might play in the catalytic behavior of the dimer warrant further investigations of these aspects of the chemistry of rhodium dimers.

This work also investigates the tetrakisocyanides 3 (p 1) and their DADPM analogs since these compounds are structurally and electronically similar to the hydrogen generating system 5 (p 4). It is of interest to determine whether the tetrakisocyanides can also produce dihydrogen and if so, what effect changing the terminal and bridging ligands has on their hydrogen generating capability.

Since the use of rhodium dimers as catalysts in hydrogenation of olefins and acetylenes and hydrogen generation involves oxidative-addition and reductive elimination, this work also investigates some aspects of the electrochemistry of some dimeric phosphine and arsine bridged complexes. The effect of various ligands on the redox potentials of these binuclear rhodium complexes is crucial to assessing their applications in catalytic processes.

CHAPTER II

EXPERIMENTAL

A. Chemicals

1. Reagents

a. Rhodium(III) trichloride trihydrate, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. Reagent grade $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Strem) was used without further purification.

b. Methyl diphenylphosphine, $\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_2$. Reagent grade $\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_2$ (Strem) was used without further purification.

c. Chlorodiphenylarsine, $\text{ClAs}(\text{C}_6\text{H}_5)_2$. Reagent grade $\text{ClAs}(\text{C}_6\text{H}_5)_2$ (Strem) was used without further purification.

d. N,N,N',N'-tetramethylethylenediamine, TMED. Electrophoretic grade TMED (Fisher) was used without further purification.

e. Sodium metal, Na. Reagent grade Na was used without additional modification.

f. n-butyllithium, $n\text{-C}_4\text{H}_9\text{Li}$. A 2.4 M solution of $n\text{-C}_4\text{H}_9\text{Li}$ (Alpha-Ventron) in hexane was used without further purification.

g. Di- μ -chloro-bis-(η^4 -1,5-cyclooctadiene)dirhodium(I), $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$. A method similar to the one employed by Giordano and Crabtree⁵⁸ was used to make $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (5.01 g, 19.0 mmol) and 1,5- C_8H_{10} (7.5 mL, 61 mmol) were refluxed together under nitrogen in degassed 83% aqueous ethanol (50 mL) for 20 hr. The mixture was cooled to room temperature and the resulting burnt-orange solid was collected by filtration and washed with pentane and 83% aqueous methanol: yield 4.26 g (45%).

h. Tetrabutylammonium chloride, $(C_4H_9)_4NCl$. This compound was made by the neutralization of 40% aqueous $(C_4H_9)_4NOH$ with 6 M HCl . The water was then stripped off under vacuum leaving a white, pasty solid. This solid was recrystallized from acetone-ether five times resulting in a white powder. This extremely hygroscopic salt was dried in vacuo at ca. $55^\circ C$.

i. Tetrabutylammonium iodide, $(C_4H_9)_4NI$. Reagent grade $(C_4H_9)_4NI$ (Aldrich) was recrystallized five times from acetone-ether and dried in vacuo.

j. Tetrabutylammonium hydroxide, $(C_4H_9)_4NOH$. A 40% aqueous solution of $(C_4H_9)_4NOH$ (Aldrich) was used without additional purification.

k. Hydrogen hexafluorophosphate, HPF_6 . A 60% aqueous solution of HPF_6 (Alpha-Ventron) was used without additional purification.

l. Potassium hexafluorophosphate, KPF_6 . Reagent grade KPF_6 (Aldrich) was used without further purification.

m. Hydrochloric acid, HCl . A.C.S. reagent grade 12 M aqueous HCl (Fisher) was used after dilution to approximately 6 M with water but without additional purification.

n. Isopropylisocyanide, $i-C_3H_7NC$. Reagent grade $i-C_3H_7NC$ (Aldrich) was stored at $0-5^\circ C$ and was used without further purification.

o. Normal butylisocyanide, $n-C_4H_9NC$. Reagent grade $n-C_4H_9NC$ (Aldrich) was stored at $0-5^\circ C$ and was used without further purification.

p. Tertiary butylisocyanide, $t\text{-C}_4\text{H}_9\text{NC}$. Reagent grade $t\text{-C}_4\text{H}_9\text{NC}$ (Aldrich) was stored at $0\text{--}5^\circ\text{C}$ and was used without additional purification.

q. Ammonium hexafluorophosphate, NH_4PF_6 . Reagent grade NH_4PF_6 (Aldrich) was used without further purification.

4. Bis(diphenylphosphino)methane, DPM. Reagent grade DPM (Strem) was used without further purification.

s. Bis(diphenylarsino)methane, DAM. Reagent grade DAM (Strem) was used without further purification.

t. Tetracarbonyl- μ -dichlorodirhodium, $\text{Rh}_2(\text{CO})_4\text{Cl}_2$. Reagent grade $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (Strem) was stored at $0\text{--}5^\circ\text{C}$ and was used without further purification.

u. Nitrosyl hexafluorophosphate, NOPF_6 . Reagent grade NOPF_6 was used without further purification.

v. Sodium thiocyanate, NaSCN . Reagent grade NaSCN (Baker) was dried at 75°C under vacuum for twelve hours prior to use.

w. Sodium cyanide, NaCN . Reagent grade NaCN (Mallinckrodt) was dried at 75°C under vacuum for twelve hours prior to use.

x. 1-Chlorobutane, $\text{C}_4\text{H}_9\text{Cl}$. Certified $\text{C}_4\text{H}_9\text{Cl}$ (Fisher) was used without additional purification.

y. Pyridine, $\text{C}_5\text{H}_4\text{N}$, (py). Certified $\text{C}_5\text{H}_4\text{N}$ (Fisher) was stored approximately two weeks over KOH and distilled immediately before use from BaO according to Gordon and Ford.⁵⁹

z. 1-Butylpyridinium chloride, $[(\text{C}_5\text{H}_4\text{N})\text{C}_4\text{H}_9]\text{Cl}$. This compound was produced by a method presented by Gale and coworkers.⁶⁰ A 1:1

molar ratio of C_5H_4N and C_4H_9Cl were refluxed together for 48 hours, resulting in a dark red solution. Upon cooling the solution, a yellow-brown solid precipitated. This solid was recrystallized four times from hot CH_3CN -ethylacetate and dried in vacuo. The resulting product was a white powder with melting point 131.0° (Lit. $131.5^\circ C$).⁶⁰

aa. Tetrabutylammonium hexafluorophosphate, $(C_4H_9)_4NPF_6$. The salt $C_4H_9NPF_6$ was made either by neutralization of $(C_4H_9)_4NOH$ with HPF_6 or by metathesis of $(C_4H_9)_4NI$ and KPF_6 in water. In both cases the precipitated $(C_4H_9)_4NPF_6$ was recrystallized five times from acetone-water.

bb. Tetrabutylammonium tetrafluoroborate, $(C_4H_9)_4NBF_4$. Reagent grade $(C_4H_9)_4NBF_4$ (Aldrich) was recrystallized five times from methanol-water.

cc. 4-(Dimethylamino)pyridine, $4-(CH_3)_2N(py)$. Reagent grade $4-(CH_3)_2N(py)$ (Aldrich) was used without further purification.

dd. 3,4-Dimethylpyridine, $3,4-(CH_3)_2(py)$. Reagent grade $3,4-(CH_3)_2(py)$ (Aldrich) was used without further purification.

ee. 4-Ethylpyridine, $4-C_2H_5(py)$. Reagent grade $4-C_2H_5(py)$ (Aldrich) was used without further purification.

ff. 4-Benzoylpyridine, $4-benzoyl(py)$. Reagent grade $4-benzoyl(py)$ (Aldrich) was used without further purification.

gg. 4-Cyanopyridine, $4-CN(py)$. Reagent grade $4-CN(py)$ was used without further purification.

hh. 3-Cyanopyridine, $3-CN(py)$. Reagent grade $3-CN(py)$ was used without further purification.

ii. 1,5-Cyclooctadiene, C₈H₁₂. Reagent grade C₈H₁₀ was used without further purification.

jj. Sodium sulfate, Na₂SO₄. Certified anhydrous Na₂SO₄ (Fisher) was used without further purification.

kk. Barium oxide, BaO. Certified BaO (Fisher) was used without further purification.

ll. Potassium hydroxide, KOH. Certified KOH (Fisher) was used without additional modification.

mm. Tetrahydrofuran, THF. Certified THF (Fisher) was stored over KOH and then distilled from calcium hydride.

nn. Tetrabutylammonium dibromodicarbonyl rhodium(I), [RhBr₂(CO)₂](C₄H₉)₄. A solution of RhCl₃·3H₂O (201 mg, 0.76 mmol) in aqueous ethanol was refluxed under CO for 4 h and then it was acidified with 1 mL of 12 M HCl. Tetrabutylammonium chloride (251 mg, 0.90 mmol) was then added and the volume reduced under vacuum until a yellow precipitate appeared. The yellow solid was collected, washed with 10% aqueous HCl, and dissolved in 10 mL of cold (0°C) methanol. Concentrated HBr (2 mL) was then added and the volume reduced under vacuum until a yellow-brown precipitate formed. The solid was collected and washed with water. Yield: 224 mg (52%).

oo. Lithium chloride, LiCl. Reagent grade LiCl (Fisher) was used without further purification.

pp. Hydrobromic acid, HBr. Reagent grade HBr (Fisher) was used without further purification.

2. Gases

- a. Argon, Ar. Prepurified Ar (Selox or Burdett) was used without additional modification.
- b. Carbon monoxide, CO. Prepurified CO (Matheson or Burdett) was used without further modification.
- c. Carbon-13 enriched carbon monoxide, ^{13}CO . Isotope enriched (90%) ^{13}CO (Monsanto) was used without further purification.
- d. Chlorine, Cl_2 . Prepurified Cl_2 (Matheson) was used without further purification.
- ee. Hydrogen, H_2 . Prepurified H_2 (Burdett) was used without further purification.
- f. Nitrogen, N_2 . Prepurified N_2 (Selox or Burdett) was used without further purification.

3. Solvents

a. Synthesis

1. Ethyl ether, ether. Fresh A.C.S. reagent grade ether (Fisher) was checked for peroxides according to a procedure by Gordon and Ford⁵⁹ and, in the absence of peroxides, was used without further purification.
2. Acetone. Certified A.C.S. acetone (Fisher) was stored over 4Å molecular sieves and distilled when used for the recrystallization of $(\text{C}_4\text{H}_9)_4\text{NCl}$. For all other procedures it was used without further purification.
3. Methanol. Certified A.C.S. methanol (Fisher) was used without further purification.

4. Ethanol. Reagent grade ethanol (Aaper) was used without additional purification.

5. Toluene. Certified A.C.S. toluene (Fisher) was used without additional purification.

6. Benzene. Certified A.C.S. benzene (Fisher) was used without further purification.

7. Acetonitrile, CH₃CN. Reagent grade CH₃CN (Fisher) was used without further purification.

8. Dichloromethane, CH₂Cl₂. Certified A.C.S. CH₂Cl₂ (Fisher) was used without further purification.

9. Ethyl acetate. Certified A.C.S. ethyl acetate (Fisher) was used without further purification.

10. Double-distilled water, water. Departmental distilled water was distilled again using a WS-2 continuous water still (Kontes glass).

11. n-Propanol. Reagent grade n-propanol (Mallinckrodt) was used without further purification.

12. Pentane. Reagent grade pentane (Eastman) was used without additional purification.

b. Spectra and electrochemistry

1. Dichloromethane, CH₂Cl₂. Spectranalyzed grade CH₂Cl₂ (Fisher) was used without further purification.

2. Acetonitrile, CH₃CN. Gold label spectrophotometric grade CH₃CN (Aldrich) was used without further purification.

B. Instrumentation

1. Spectroscopy

a. Ultraviolet-visible spectroscopy (UV-Vis). UV-Vis spectra were recorded in a double beam mode on either a Cary 17 or a Cary 219 spectrophotometer. Square quartz cells (Fisher) of 1.0 cm path length were used. The cells were modified for use with air-sensitive compounds by the attachment of 8 mm O.D. quartz tubing to the cells. This configuration of the cells allowed them to be sealed with rubber septa. The cells were evacuated and the solution to be analyzed was added via syringe. All solvents used for UV-Vis spectra were deoxygenated either by bubbling with Ar for 15 minutes or by several freeze/thaw cycles.

b. Infra-red spectroscopy (IR). IR spectra were recorded on a Digilab FTS-20 C/V Fourier transform spectrometer. Samples were prepared either as KBr pellets or Nujol mulls. Certified A.C.S. KBr (Fisher) was dried at approximately 110°C for two hours immediately before use. Nujol, extra heavy mineral oil (Plough, Inc.) was dried over fused Na before use. The Nujol mulls were sealed between two sheets of "Handi-Wrap" polyethylene film (Dow) with a Clamco Super Bag Sealer.

c. Nuclear magnetic resonance spectroscopy (NMR). NMR spectra were recorded on a JEOL FX 90Q Fourier transform spectrometer. The ^1H spectra were recorded at 36.19 MHz with 85% H_3PO_4 (Fisher) as an external reference. The ^{13}C spectra were recorded at 22.51 MHz

with $(\text{CH}_3)_4\text{Si}$ (Norell) as the reference. All NMR spectra were run with the instrument locked on the deuterium signal of the solvent (CD_2Cl_2 , CDCl_3 , or $(\text{CD}_3)_2\text{CO}$). All solvents were deoxygenated by the same methods discussed above in the section on UV-Vis spectroscopy.

2. Electrochemistry

a. Electrolysis and voltammetry. Bulk electrolysis and coulometry were performed at constant potential on either a Princeton Applied Research (PAR) 173 potentiostat/galvanostat fitted with a PAR 179 digital coulometer or a PAR 363 potentiostat/galvanostat in conjunction with a digital coulometer (Electrosynthesis, Model 640). Voltammetry was performed with the PAR 363 potentiostat and a wave generator of the design of Woodward et al.⁶¹ built by the departmental electronics shop. A Houston Instruments 2000 Omnigraphic X-Y recorder was used to record all voltammograms.

b. Electrodes. Bulk electrolyses were performed with a 25 cm^3 platinum grid working electrode and a carbon rod counter electrode. Cyclic voltammetry was performed with a Beckman platinum-inlay button working electrode and a platinum grid counter electrode approximately 3 cm^2 . The reference for all electrochemical measurements was the saturated calomel electrode (SCE).

c. Cells. An H-shaped three-compartment cell was employed for all electrolyses. The cell compartments were separated by fine glass frits. The compartment in which the oxidation or reduction of interest was performed was fitted with a glass frit and stopcock so that Ar could either be bubbled through, or passed over, the solvent

in order to exclude oxygen. In this manner the same cell could be used for both bulk electrolysis and cyclic voltammetry of a given system.

In the case where only voltammetry without bulk electrolysis was desired, a standard single compartment cell was used which was designed to allow Ar to be passed either through or over the solution. All voltammetry using this cell was performed at room temperature except for the investigation of the coordination of substituted pyridines to rhodium complexes, in which case the cell was placed in a constant temperature water bath (E. H. Sargent and Co.) maintained at $25.0 \pm 0.1^\circ\text{C}$.

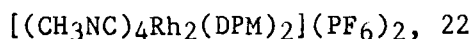
Low temperature voltammetry was performed in a two-compartment cell based on the design of Van Duyne and Reilly.⁶² The chamber containing the working and counter electrodes was surrounded by a glass jacket through which chilled N_2 was passed. The N_2 was cooled by passing it through a copper coil immersed in liquid nitrogen. The flow rate of the N_2 was used to regulate the temperature of the solution in the inner compartment. The inner chamber temperature was monitored with an iron-constantan thermocouple inserted directly into the analyte solution. The thermocouple was used in conjunction with a Fluke Model 2100A digital thermometer. The reference electrode was in a compartment outside the cooling jacket and was kept at room temperature.

All three electrochemical cells discussed above were fitted with teflon caps containing holes for electrodes and for the venting of Ar to the atmosphere.

3. Photolysis

Photolysis of rhodium complexes was done by means of a short arc xenon lamp (Varian) fitted with a 520 nm band pass filter (Oriel).

C. Production and Detection of Hydrogen from



1. Blank Runs

Zinc dust (0.017 g, 0.26 mmol) was placed in the reaction vessel shown in Figure 2 and the system was evacuated by opening swagelok valves A and B. Valve A was then closed and 1 mL of H₂SO₄ (conc.) was added to the Zn. After effervescence ceased, the reaction vessel was cooled in liquid nitrogen and the gases present in the reaction and observation tubes were excited by means of an arc discharge from a tesla coil (Electro Technique Products) directed onto the metal swagelok valve A. When valve A was opened, the red H emission line at 656.28 nm was readily observed in the observation tube with a prismatic spectroscope (Bausch and Lomb). The appearances of the H line upon opening valve A was again checked by a process similar to that described above except that commercial H₂ was introduced into the reaction vessel.

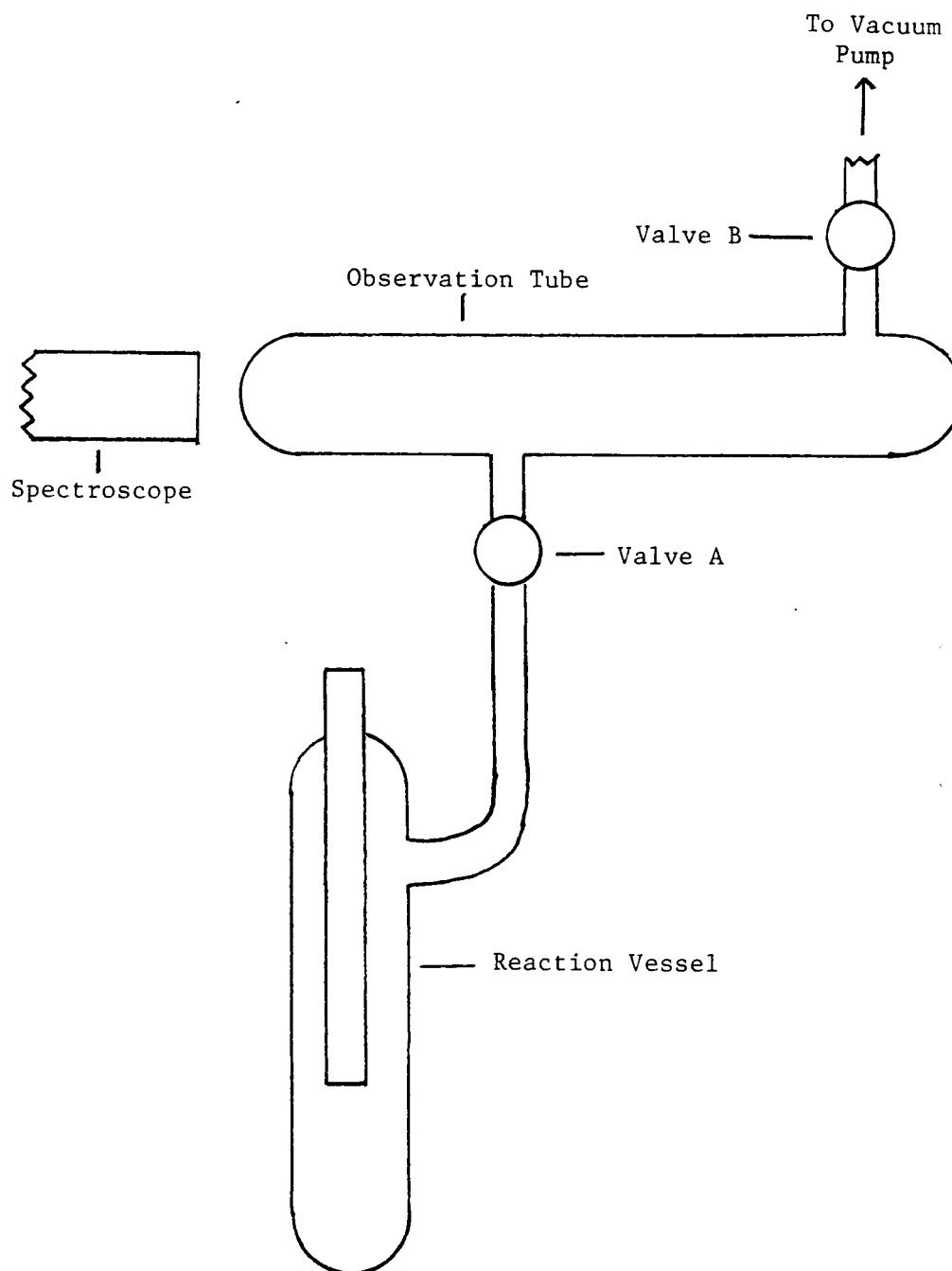


Figure 2. Experimental set-up for detecting hydrogen evolution from binuclear rhodium complexes.

A solvent blank was run by introducing 2 mL of a 25-volume percent solution of water in acetone to the evacuated reaction tube in Figure EX-1 and freezing the solution at 77K. Spectral analysis of the glow discharge in this case did not show the red H line upon opening valve A.

2. Production of Hydrogen from $[\text{Rh}_2(\text{CH}_3\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 22. The deep blue complex 22 (0.169 g, 0.116 mmol) was placed into the reaction vessel shown in Figure 2 and the system was evacuated. No background H lines were seen at this point upon excitation of the system. Valve A was then closed and 2 mL of a 25-volume percent solution of water in acetone was added to the reaction vessel, producing a rose-red mixture. This mixture was frozen in liquid nitrogen and the system was excited with the tesla coil. No H lines were observed with valves A and B closed, but the 652.28 nm H line was readily seen in the observation tube upon opening valve A. The red hydrogen line was also detected with a similar procedure using the tetraphenyl borate analogue of complex 22.

D. Elemental Analysis

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

E. Synthesis

1. (Diphenylarsino)(diphenylphosino)methane, (C₆H₅)₂AsCH₂P(C₆H₅)₂, DADPM

A method similar to the one used by Grimm and Mitchell⁶³ was employed to make DADPM. TMED (22.2 g, 191 mmol) was added dropwise under nitrogen to a rapidly stirred solution of 79.5 mL of 2.4 M n-butyllithium in hexane. To this yellow solution was added methyldiphenylphosphine (38.2 g, 191 mmol), and after about 10 min a yellow precipitate was formed. The slurry was stirred for 3 h, after which 75 mL of THF was added, yielding a deep red solution. This solution was added dropwise under nitrogen to a solution of 50.5 g (191 mmol) of chlorodiphenylarsine in 50 mL of benzene. The resulting orange slurry was refluxed 1 h and allowed to stir ca. 10 h. The mixture was reduced in volume and the resulting oil was dissolved in 150 mL of dichloromethane. The dichloromethane solution was washed with four 100-mL portions of water to extract the lithium chloride. The dichloromethane layer was dried over Na₂SO₄, after which the solvent was removed under vacuum, yielding a heavy oil. Crystallization from hot ethanol produced white crystals. Yield: 27.0 g (33%).

³¹P{¹H} NMR spectrum: $\delta = -23.3$ ppm (from 85% H₃PO₄). Anal. calcd. for C₂₅H₂₂AsP: C, 70.10; H, 5.18; P, 7.23. Found: C, 69.74; H, 5.10; P, 7.17.

2. Dicarbonyldichlorobis[μ -[[diphenylarsino)methyl]diphenylphosphine-As:P]]dirhodium(I), $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DADPM})$, 29

A method employed by Mague and Mitchener¹ was used to prepare 29.

A mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1.00 g, 3.8 mmol) in 200 mL of aqueous ethanol was refluxed under carbon monoxide ca. 4 h until it became lemon yellow. This solution was cooled to room temperature, and a solution of $(\text{C}_6\text{H}_5)_2\text{AsCH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (1.63 g, 3.8 mmol) in a minimum volume of acetone was added. The orange precipitate that appeared upon rapid stirring was collected by filtration and washed with ether. Yield: 1.76 g (77%).

IR spectrum: $\nu(\text{CO})$ in KBr = 1967 cm^{-1} (S). $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: $\delta = 27.3$ ppm (from 85% H_3PO_4); $J(\text{Rh-P}) = 149$ Hz. UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]: 455 nm (6740), 283 (Sh) (17,300). Anal. Calcd. for $\text{C}_{52}\text{H}_{44}\text{As}_2\text{Cl}_2\text{O}_2\text{P}_2\text{Rh}_2$: C, 52.50; H, 3.72; P, 5.20. Found: C, 53.12; H, 3.85; P, 5.51.

3. ^{13}C analogue of 29, $\text{Rh}_2(^{13}\text{CO})_2\text{Cl}_2(\text{DADPM})_2$

This compound was made according to the procedure used for complex 29. Using $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (206 mg, 0.78 mmol), DADPM (334 mg, 0.78 mmol), and 90 percent enriched ^{13}CO produced 356 mg of $\text{Rh}_2(^{13}\text{CO})_2(\text{DADPM})_2$ (77%).

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum: $\delta = 188$ ppm [from $(\text{CH}_3)_4\text{Si}$], $^1J(\text{Rh-C}) = 73$ Hz, $^2J(\text{Rh-C}) = 14$ Hz. IR spectrum: $\nu(\text{CO})$ in Nujol = 1924 cm^{-1} (S) and 1971 cm^{-1} (W).

4. Dicarbonyldichlorobis[μ -methylenebis[diphenylphosphine]-
P:P']dirhodium(I), $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DPM})_2$, 1

Complex 1 was either obtained from Tinsley⁶⁴ or was made by method c reported by Mitchener.¹ Using 523 mg (2.0 mmol) of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 774 mg (2.0 mmol) of DPM in the same procedure described above, 0.678 g of 1 (62%) was obtained.

IR spectrum: $\nu(\text{CO})$ in KBr = 1971 cm^{-1} (S).

5. Dicarbonyldichlorobis[μ -methylenebis[diphenylarsine]-
As:As']dirhodium(I), $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DAM})_2$, 2

This compound was either supplied by Tinsley⁶⁴ or made according to the procedure given for complex 29. Using 502 mg (1.9 mmol) of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 902 mg (1.9 mmol) of DAM, 0.706 g of 2 (58%) was obtained.

IR spectrum: $\nu(\text{CO})$ in KBr = 1962 cm^{-1} (Lit.² 1963 cm^{-1} [solid]).

6. Tetrakis(2-isocyano-2-methylpropane)bis[μ -methylenebis]diphenyl
phosphine]-P;P']dirhodium(I) bis[hexafluorophosphate],
 $[\text{Rh}(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 23

This complex was made according to a procedure reported by Balch⁵ et al. A methanol solution of 1.485 g (17.9 mmol) of $\text{t-C}_4\text{H}_9\text{NC}$ was added dropwise to a briskly stirred solution of $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ (2.205 g, 4.5 mmol) and DPM (3.435 g, 8.4 mmol) in ca. 100 mL of deoxygenated methanol. The deep red-blue solution was stirred for 45 min and filtered. A solution of NH_4PF_6 (1.458 g, 8.9 mmol) in ca. 15 mL methanol was then added, resulting in a maroon precipitate. The

mixture was stirred for 1 h and a red solid was collected by filtration and recrystallized from CH_2Cl_2 and *n*-propanol. Yield: 4.59 g (64%).

IR spectrum: $\nu(\text{CN})$ in Nujol = 2124 cm^{-1} (S) and 2154 cm^{-1} (W) (Lit.² 2122 and 2152 cm^{-1} [solid]). UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]; 519 nm (18,700), 335 (Sh) nm (15,000), 320 nm (28,600) (Lit.² [in CH_3CN] 523 nm (22,000), 337 nm (14,300), 320 nm (20,200)).

7. Tetrakis(2-isocyanopropane)bis[μ -methylenebis[diphenylphosphine]-P:P']dirhodium(I) bis[hexafluorophosphate], $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 25

Compound 25 was produced by the same procedure used to make complex 23. Using 1.783 g (3.6 mmol) of $[\text{RhCl}(\text{C}_6\text{H}_5)_2]_2$, 2.781 g (7.2 mmol) of DPM, 997 mg (14.4 mmol) of *i*- $\text{C}_3\text{H}_7\text{NC}$, and 1.182 g (7.2 mmol) of NH_4PF_6 , 2.04 g of 25 (37%) was obtained.

IR spectrum: $\nu(\text{NC})$ in Nujol = 2150 cm^{-1} (M) and 2175 cm^{-1} (W). UV-Vis spectrum [λ_{max} (ϵ)]; 545 nm (10,300); 384 nm (2140), 340 nm (Sh) (7360), 319 nm (13,700). Anal. calcd. for $\text{C}_{66}\text{H}_{72}\text{N}_4\text{P}_4\text{Rh}_2\cdot\text{F}_{12}\text{P}_2$: C, 51.44; H, 4.71; N, 3.64. Found: C, 51.03; H, 4.78; N, 3.73.

8. Tetrakis(2-isocyanopropane)bis[μ -methylenebis[diphenylphosphine]-P:P']dirhodium(I) bis[tetrafluoroborate], $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{BF}_4)_2$, 26

The same method was used to prepare this complex as was used to make 23. Using $[\text{RhCl}(\text{C}_6\text{H}_5)_2]_2$ (4.061 g, 8.2 mmol), DPM (6.304 g, 16.4

mmol), i-C₃H₇NC (2.277 g, 27.4 mmol), and (C₄H₉)₄NBF₄ (5.425 g, 16.5 mmol), 5.44 g of 26 (46%) was obtained.

IR spectrum: $\nu(\text{CN})$ in Nujol = 2147 cm⁻¹ (M) and 2169 cm⁻¹ (W).

9. Tetrakis(2-isocyanobutane)bis[μ -methylenebis[diphenylphosphine]-P:P']dirhodium(I)bis[hexafluorophosphate],
[Rh₂(n-C₄H₉NC)₄(DPM)₂](PF₆)₂, 27

The same method was used to prepare this complex as was used to make 23. Using [RhClC₈H₁₂]₂ (1.258 g, 2.6 mmol), n-C₄H₉NC (0.849 g, 10.2 mmol), DPM (1.961 g, 5.1 mmol) and NH₄PF₆ (8.32 mg, 5.1 mmol), 1.65 g of 27 (40%) was obtained.

IR spectrum in Nujol: $\nu(\text{CN})$ in Nujol = 2160 cm⁻¹ (S) and 2185 cm⁻¹ (Sh) (lit.² 2146 cm⁻¹ and 2165 cm⁻¹ [solid for the tetraphenylborate salt]. UV-Vis spectrum in CH₂Cl₂ [λ_{max} (ϵ): 546 nm (12,900), 390 nm (2300), 335 nm (Sh) (10,300), 318 nm (18,600) [Lit.² in CH₃CN: 560 nm (12,200), 340 (Sh) (5800), 316 nm (18,100)]. Anal. calcd. for C₇₀H₈₀P₄Rh₂N₄•F₁₂P₂: C, 52.56; H, 5.22; P, 11.90. Found: C, 52.6; H, 5.05; P, 11.64.

10. μ -Carbonyldicarbonyl- μ -chlorobis[μ -[(diphenylarsino)methyl]diphenylphosphine-As:P]]dirhodium(I) hexafluorophosphate,
[Rh₂(μ -CO)(CO)₂(μ -Cl)(DADPM)₂](PF₆)₂, 32

A mixture of RhCl₃•3H₂O (200 mg, 0.76 mmol) in aqueous ethanol was refluxed under CO for 4 h. The CO was bubbled through the solution during the reflux process. To the yellow solution were added DADPM (326 mg, 0.76 mmol) in 4 mL THF and NH₄PF₆ (126 mg, 0.77 mmol) in 3 mL of ethanol in quick succession. The resulting orange

precipitate was collected by filtration under CO and washed with water, ethanol, and ether. Yield 374 mg (74%). The solid product loses CO overnight to produce complex 35.

IR spectrum: $\nu(\text{CO})$ in Nujol = 1981 cm^{-1} (M), 1967 cm^{-1} (M), and 1843 cm^{-1} (W).

11. Dicarbonyl- μ -chlorobis[μ -[[diphenylarsino)methyl]diphenylphosphine-As:P]]dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DADPM})_2](\text{PF}_6)_2$, 35

This compound was made by dissolving complex 32 in a 2.5:1 mixture of THF/acetone and bubbling it with N_2 for 10 minutes. Equal volumes of ether and ligroin were added until the cloud point was reached, and the mixture was cooled to 0°C for 90 minutes. The resulting orange solid was collected by filtration and washed with ether. The yield for this reaction is quantitative.

IR spectrum: $\nu(\text{CO})$ in Nujol = 1981 cm^{-1} (S) and 1965 cm^{-1} (S).
UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ): 435 nm (10,600), 305 nm (Sh) (12,700)]. Anal. calcd. for $\text{C}_{52}\text{H}_{44}\text{As}_2\text{ClP}_2\text{Rh}_2\cdot\text{F}_6\text{P}$: C, 48.08; H, 3.41; Cl, 2.73. Found: C, 49.06; H, 3.91; Cl, 6.18.

12. Bromo- μ -carbonyldicarbonylbis[μ -[[diphenylarsino)methyl]diphenylphosphine-As:P]]dirhodium(I) bromide, $[\text{Rh}_2\text{Br}(\mu\text{-CO})(\text{CO})_2(\text{DADPM})_2]\text{Br}$, 38

The ligand DADPM (171 mg, 0.40 mmol) was added in benzene to a solution of $[\text{RhBr}_2(\text{CO})_2]\text{N}(\text{C}_4\text{H}_9)_4$ (223 mg, 0.40 mmol). The resulting

yellow compound was precipitated by the addition of ether, collected by filtration and washed with ether. Yield: 176 mg (65%).

IR spectrum: $\nu(\text{CO})$ in Nujol = 1998 cm^{-1} (M), 1952 cm^{-1} (M), and 1869 cm^{-1} (M). UV-Vis spectra in CH_2Cl_2 [λ_{max} (ϵ)]: 447 nm (3900), 344 nm (8270), 290 (Sh) (16,900).

13. Dicarbonylchloro(2-isocyano-2-methylpropane)bis[μ -[[diphenyl-arsino)methyl]diphenylphosphine-As:P]]dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\text{CO})_2\text{Cl}(\text{t-C}_4\text{H}_9\text{NC})(\text{DADPM})_2](\text{PF}_6)$, 44

A solution of $\text{t-C}_4\text{H}_9\text{NC}$ (7.64 mg, 0.092 mmol) in acetone was added to a rapidly stirred solution of compound 35 (116 mg, 0.092 mmol) in 5 mL of acetone under CO. An orange precipitate appeared upon addition of 3 mL of ether and 8 mL of ligroin. The mixture was cooled to 0°C , and the solid was collected by filtration under CO. Yield: 101 mg (71%).

IR spectrum in Nujol: $\nu(\text{CN}) = 2209\text{ cm}^{-1}$ (M), $\nu(\text{CO}) = 2005\text{ cm}^{-1}$ (S) and 1954 cm^{-1} (S). UV-Vis spectrum in CH_2Cl_2 [λ_{max} , (ϵ)]: 443 nm (5750), 380 nm (3700), 305 nm (Sh) (10,200). Anal. calcd. for $\text{C}_{57}\text{H}_{53}\text{As}_2\text{Cl}_2\text{NOP}_2\text{Rh}_2\cdot\text{F}_6\text{P}$: C, 49.54; H, 3.87; N, 1.01; Cl, 2.57. Found: C, 49.08; H, 3.96; N, 0.86; Cl, 2.71.

14. Carbonylchlorobis(2-isocyano-2-methylpropane)bis[μ -[[diphenyl-arsino)methyl]diphenylphosphine-As:P]]dirhodium(I) hexafluorophosphate, $[\text{Rh}_2(\text{CO})\text{Cl}(\text{t-C}_4\text{H}_9\text{NC})_2(\text{DADPM})_2](\text{PF}_6)$, 45

Compound 45 was produced by the same procedure used to make complex 44. Using $\text{t-C}_4\text{H}_9\text{NC}$ (15.6 mg, 0.19 mmol) and compound 35 (122

mg, 0.094 mmol) produced 101 mg of 45 (70%).

IR spectrum in Nujol: $\nu(\text{CN}) = 2120 \text{ cm}^{-1}$ (S), $\nu(\text{CO}) = 1954 \text{ cm}^{-1}$ (S). UV-Vis spectrum in CH_2Cl_2 [$\lambda_{\text{max}} (\epsilon)$]: 515 nm (3650), 458 nm (4860), 383 nm (3540), 302 (Sh) (12,000). Anal. calcd. for $\text{C}_{61}\text{H}_{62}\text{As}_2\text{Cl}_2\text{ONRh}_2 \cdot \text{F}_6\text{P}$: C, 50.98; H, 4.35; N, 1.95; Cl, 2.47. Found: C, 50.43; H, 4.37; N, 1.81; Cl, 2.62.

15. Tetrakis(isocyanocyclohexane)bis[μ -[[[(diphenylarsino)methyl]diphenylphosphine-As:P]]dirhodium(I) bis[hexafluorophosphate], $[\text{Rh}_2(\text{c-C}_6\text{H}_{11}\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$, 47

The procedure for preparing 47 is analogous to that used to prepare similar DAM and DPM complexes.¹⁸ A solution of c-C₆H₁₁NC (167 mg, 1.53 mmol) in 3 mL of methanol was added dropwise to a stirred slurry of compound 29 (454 mg, 0.38 mmol) in 50 mL of methanol. The deep purple solution was stirred for 20 min, and NH_4PF_6 (126 mg, 0.77 mmol) in 5 mL of methanol was added. Reddish purple crystals precipitated after 10 min. of stirring and were collected by filtration. The product was recrystallized from acetone/n-propanol. Yield: 168 mg (25%).

IR spectrum: $\nu(\text{NC})$ in Nujol = 2166 cm^{-1} (M), 2137 cm^{-1} (S). UV-Vis spectrum in CH_2Cl_2 [$\lambda_{\text{max}} (\epsilon)$]: 548 nm (1500), 322 nm (1300), 265 nm (Sh) (20,600). Anal. calcd. for $\text{C}_{78}\text{H}_{88}\text{As}_2\text{N}_4\text{P}_2\text{Rh}_2 \cdot \text{F}_{12}\text{P}_2$: C, 52.36; H, 4.96; N, 3.13; P, 6.92. Found: C, 52.65; H, 5.16; N, 3.11; P, 7.26.

16. Tetrakis(2-isocyanopropane)bis[μ -[[diphenylarsino)methyl]diphenylphosphine-As:P]]dirhodium(I) bis(hexafluorophosphate), $\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DADPM})_2(\text{PF}_6)_2$, 46

The same method was used to make this complex as was used to make compound 47. Using i-C₃H₇NC (116 mg, 1.68 mmol), compound 29 (499 mg, 0.42 mmol), and NH₄PF₆ (153 mg, 0.94 mmol) yielded 134 mg (20%) of complex 46.

IR spectrum: $\nu(\text{CN})$ in Nujol = 2144 (S). UV-Vis spectrum in CH₂Cl₂ [λ_{max} (ϵ)]: 545 nm (9160), 322 nm (13,000), 246 nm (Sh) (13,400). ³¹P{¹H} NMR spectrum: δ = 25.7 ppm (from 85% H₃PO₄), ¹J(Rh-P) = 144 Hz. Anal. calcd. for C₆₆H₄₂As₂N₄P₂Rh₂·F₁₂P₂: C, 48.66; H, 4.46; N, 3.44. Found: C, 47.56; H, 4.30; N, 3.26.

17. Tetrakis(2-isocyano-2-methylpropane)bis[μ -[[diphenylarsino)methyl]disphosphine-As:P]]dirhodium(I) bis(hexafluorophosphate), $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$, 48

The same method was used to produce compound 45 as was used to make complex 47. Using t-C₄H₉NC (128 mg, 1.5 mmol), complex 29 (459 mg, 0.39 mmol), and NH₄PF₆ (127 mg, 0.78 mmol) produced 277 mg (43%) of red 48.

IR spectrum: $\nu(\text{NC})$ in Nujol = 2153 cm⁻¹ (S), 2125 cm⁻¹ (S). UV-Vis spectrum in CH₂Cl₂ [λ_{max} (ϵ)]: 517 nm (11,300), 385 nm (4650), 323 nm (14,500), 265 nm (16,300). ³¹P{¹H} NMR spectrum: δ = 25.5 ppm (from 85% H₃PO₄), ¹J(Rh-P) = 141 Hz. Anal. calcd. for C₇₀H₈₀As₂N₄P₂Rh₂·F₁₂P₂: C, 49.90; H, 4.79; N, 3.32. Found: C, 48.39; H, 4.87; N, 2.98.

18. Dicarbonyl- μ -chlorodichlorobis [μ -[[diphenylarsino)methyl] diphenylphosphine-As:P]]dirhodium(I) tetrafluoroborate, dichloromethane adduct, $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}_2(\text{DADPM})_2](\text{BR}_4)^+$ $1/2 \text{ CH}_2\text{Cl}_2$, 54

A 10^{-3} M solution of complex 29 in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$, and 10^{-2} M $(\text{C}_4\text{H}_9)_4\text{NCl}$ was oxidized at $+0.65 \text{ V}$ via controlled potential electrolysis. The CH_2Cl_2 was then removed under vacuum and the electrolysis product was separated from the $(\text{C}_4\text{H}_9)_4\text{NBF}_4$ and $(\text{C}_4\text{H}_9)_4\text{NCl}$ by stirring the mixture in hot water for ca. 10 h. The burnt-orange compound was collected by filtration, washed with water, and recrystallized twice from acetone/water. Yield: 87 mg (47%). IR spectrum: $\nu(\text{CO})$ in Nujol = 1996 cm^{-1} (S) and 1980 cm^{-1} (S). Anal. calcd. for $\text{C}_{52}\text{H}_{44}\text{As}_2\text{Cl}_3\text{O}_2\text{Rh}_2 \cdot \text{BF}_4 \cdot 1/2 \text{ CH}_2\text{Cl}_2$: C, 43.73; H, 3.14; Cl, 9.83. Found: C, 43.84; H, 3.58; Cl, 9.98.

19. Tetrakis(2-isocyanopropane)dithiocyanatobis [μ -methylenebis [diphenylphosphine]-P:P']dirhodium(II) bis(tetrafluoroborate), $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{SCN})_2(\text{DPM})_2](\text{BF}_4)_2$, 59

A CH_3CN solution of 26 (97 mg, 0.068 mmol) with 0.1 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$ present was oxidized at $+1.00 \text{ V}$ via controlled potential electrolysis. The yellow oxidation product was recovered by removing the CH_3CN under vacuum and recrystallizing the mixture twice from acetone/water. The oxidation product was dissolved in 5 mL of CH_3CN and NaSCN (12 mg, 0.15 mmol) was added in a minimum volume of CH_3CN . The resulting

compound was precipitated by the addition of water and dried in vacuo.

Yield: 13 mg (12%).

IR spectrum in Nujol: $\nu(\text{RNC}) = 2194 \text{ cm}^{-1}$ (S) and 2182 cm^{-1} (S), $\nu(\text{SCN}) = 2094 \text{ cm}^{-1}$ (M) and 2050 cm^{-1} (M). UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]: 375 nm (7470), 305 nm (Sh) (14,600) 258 nm (Sh) (27,100). Anal. calcd. for $\text{C}_{68}\text{H}_{72}\text{N}_6\text{P}_4\text{S}_2\text{Rh}_2 \cdot \text{B}_2\text{F}_8$: N, 5.45; S, 4.16. Found: N, 5.36; S, 4.11.

20. Tetrakis(2-isocyanopropane)dicyanobis[μ -methylenebis(diphenyl phosphine)-P:P']dirhodium(II) bis(tetrafluoroborate),
 $[\text{Rh}_2(1\text{-C}_3\text{H}_7\text{NC})_4(\text{CN})_2(\text{DPM})_2](\text{BF}_4)_2$, 60

A CH_3CN solution of 26 (94 mg, 0.066 mmol) with 0.1 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$ present was oxidized at +1.00 V via controlled potential electrolysis. The resulting yellow solution turned red upon addition of NaCN (7.2 mg, 0.15 mmol) in 15 mL of methanol. The solvents were removed under vacuum and the residue was dissolved in acetone. Yellow complex 60 was recovered by precipitation with water and was recrystallized from acetone/water. Yield: 72 mg (74%).

IR spectrum in Nujol: $\nu(\text{RNC}) = 2203 \text{ cm}^{-1}$. No IR bands were observed that could be assigned to the ionic CN group. UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]: 374 nm (4113), 296 nm (Sh) (13,300), 257 nm (20,500). Anal. calcd. for $\text{C}_{68}\text{H}_{72}\text{N}_6\text{P}_4\text{Rh}_2 \cdot \text{B}_2\text{F}_8$: N, 5.69. Found: N, 5.78.

21. Attempted syntheses of dichloro rhodium(II) complexes of the type $[\text{Rh}_2(\text{RNC})_4\text{Cl}_2(\text{DPM})_2]\cdot\text{X}_2$, $\text{X} = \text{PF}_6^-$, BF_4^-

Although synthesis of compounds of type 24 involving complexes containing i-propyl, t-butyl-, and n-butylisocyanide ligands were attempted, only the procedures using the i-propylisocyanide compounds 25 and 26 are illustrated. Similar results were obtained using the other compound types.

a. Synthesis involving Cl_2 . Typical syntheses of 24 involved bubbling Cl_2 through a CH_2Cl_2 solution of 25, causing an immediate color change from deep blue to pale yellow. Any excess Cl_2 present was removed by bubbling the solution with N_2 . Approximately 10 mL of n-propanol was added to the solution and the CH_2Cl_2 removed under vacuum until a yellow precipitate formed. The yellow solid was then collected and washed with methanol and ether.

Typical results: UV-Vis spectrum [λ_{max} (ϵ)]: 380 nm (20,300), 296 nm (37,800). Anal. calcd. for $\text{C}_{66}\text{H}_{72}\text{Cl}_2\text{N}_4\text{P}_4\text{Rh}_2\cdot\text{F}_{12}\text{P}_2$: C, 49.15; H, 4.50; Cl, 4.40. Found: C, 41.17; H, 3.96; Cl, 9.61.

b. Syntheses involving NOPF_6 . A solution of LiCl (17 mg, 0.040 mmol) in 10 mL of CH_3CN was added to a solution of 25 (53 mg, 0.034 mmol) in 20 mL of CH_3CN . The NOPF_6 (12.6 mg, 0.072 mmol) was then added with stirring, and the solution slowly changed to pale yellow. The CH_3CN was removed under vacuum and the yellow product recrystallized from acetone/water.

Typical results: IR spectrum: $\nu(\text{CN})$ in Nujol = 2196 cm^{-1} (S).
 UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]: 395 nm (1600), 305 nm (Sh) (5200), 270 nm (6640). Anal. calcd. for $\text{C}_{66}\text{H}_{72}\text{Cl}_2\text{N}_4\text{P}_4\text{Rh}_2\cdot\text{F}_{12}\text{P}_2$: N, 3.48; Cl, 4.40. Found: N, 3.72; Cl, 2.71.

c. Syntheses involving photolysis. A 10^{-3} M solution of 26 in CH_2Cl_2 with $4 \times 10^{-3}\text{ M}$ $(\text{C}_4\text{H}_9)_4\text{NCl}$ present was photolyzed at 520 nm until it turned pale yellow (ca. 4 h). The CH_2Cl_2 was removed under vacuum and the photolysis product was recrystallized from acetone/water.

Typical results: IR spectrum: $\nu(\text{NC})$ in Nujol = 2192 cm^{-1} (W).
 UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]: 481 nm (6200), 304 nm (18,900), 260 nm (27,000). Anal. calcd. for $\text{C}_{66}\text{H}_{72}\text{Cl}_2\text{N}_4\text{P}_4\text{Rh}_2\cdot\text{B}_2\text{F}_8$: N, 3.75; Cl, 4.74. Found: N, 3.48; Cl, 0.60.

d. Syntheses involving electrolyses. A 10^{-3} M solution of 25 in CH_2Cl_2 with 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ and $4 \times 10^{-3}\text{ M}$ $[(\text{C}_5\text{H}_4\text{N})\text{C}_4\text{H}_9]\text{Cl}$ present was oxidized at +0.700 V via controlled potential electrolysis. The CH_2Cl_2 was removed under vacuum from the resulting yellow solution. The residue was stirred with methanol and filtered three times and washed five times with methanol and dried in vacuo.

Typical results: IR spectrum: $\nu(\text{CN})$ in Nujol = 2212 cm^{-1} (M) and 2229 cm^{-1} (M). UV-Vis spectrum in CH_2Cl_2 [λ_{max} (ϵ)]: 383 nm (17,200), 305 nm (Sh) (27,300), 267 nm (33,800). Anal. calcd. for $\text{C}_{66}\text{H}_{72}\text{Cl}_2\text{N}_4\text{P}_4\text{Rh}_2\cdot\text{F}_{12}\text{P}_2$: C, 49.12; H, 4.50; N, 3.48; Cl, 4.40. Found: C, 47.04; H, 4.22; N, 2.75; Cl, 6.80.

F. Compound Identification

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

TABLE I
COMPOUND IDENTIFICATION

Compound number	Compound
1	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DPM})_2$
2	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DAM})_2$
3	$[\text{Rh}_2(\text{RNC})_2(\text{DPM})_2]^{2+}$
5	$[\text{Rh}_2(\text{bridge})_4]^{2+}$
8	$\text{Rh}_2(\text{CO})\text{Cl}_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4\text{N})]_2$
9	$\text{Rh}_2(\mu\text{-CO})\text{Cl}_2(\text{DPM})_2$
20	$[\text{Rh}_2\text{Cl}_2(\text{bridge})_4]^{2+}$
21	$[\text{Rh}_2\text{Cl}_2(\text{bridge})_4]^{4+}$
22	$[\text{Rh}_2(\text{CH}_3\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$
23	$[\text{Rh}_2(\underline{\text{t}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$
24	$[\text{Rh}_2\text{Cl}_2(\text{RNC})_4(\text{DPM})_2](\text{PF}_6)_2$
25	$[\text{Rh}_2(\underline{\text{i}}\text{-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$
26	$[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{BF}_4)_2$
27	$[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$
28	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DADPM})_2$ (HH)
29	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DADPM})_2$ (HT)
30	$[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2]^+$
31	$[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-Cl})(\text{DAM})_2]^+$
32	$[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-Cl})(\text{DADPM})_2]^+$
33	$[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2]^+$

TABLE I (Continued)

Compound number	Compound
34	$[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DAM})_2]^+$
35	$[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DADPM})_2]^+$
36	$[\text{Rh}_2\text{Br}(\mu\text{-CO})(\text{CO})_2(\text{DPM})_2]\text{Br}$
37	$[\text{Rh}_2\text{Br}(\mu\text{-CO})(\text{CO})_2(\text{DAM})_2]\text{Br}$
38	$[\text{Rh}_2\text{Br}(\mu\text{-CO})(\text{CO})_2(\text{DADPM})_2]\text{Br}$
39	$\text{Rh}_2\text{Br}_2(\text{CO})_2(\text{DAM})_2$
40	$[\text{Rh}_2(\mu\text{-CO})(\text{CO})\text{Cl}(\underline{\text{t}}\text{-C}_4\text{H}_9\text{NC})(\text{DPM})_2]^+$
41	$[\text{Rh}_2(\text{CO})_2\text{Cl}(\underline{\text{t}}\text{-C}_4\text{H}_9\text{NC})(\text{DAM})_2]^+$
42	$[\text{Rh}_2(\mu\text{-CO})\text{Cl}(\underline{\text{t}}\text{-C}_4\text{H}_9\text{NC})_2(\text{DPM})_2]^+$
43	$[\text{Rh}_2(\text{CO})\text{Cl}(\underline{\text{t}}\text{-C}_4\text{H}_9\text{NC})_2(\text{DAM})_2]^+$
44	$[\text{Rh}_2(\text{CO})_2\text{Cl}(\underline{\text{t}}\text{-C}_4\text{H}_9\text{NC})(\text{DADPM})_2]\text{PF}_6$
45	$[\text{Rh}_2(\text{CO})\text{Cl}(\underline{\text{t}}\text{-C}_4\text{H}_9\text{NC})_2(\text{DADPM})_2](\text{PF}_6)_2$
46	$[\text{Rh}_2(\underline{\text{i}}\text{-C}_3\text{H}_7\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$
47	$[\text{Rh}_2(\text{C}_6\text{H}_{11}\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$
48	$[\text{Rh}_2(\underline{\text{t}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$
49	$\text{Rh}_2(\text{CO})_2\text{Cl}_2\text{I}_2(\text{DPM})_2$
50	$\text{Rh}_2\text{Br}_4(\text{CO})_2(\text{DAM})_2$
51	$\text{Rh}_2\text{Br}_2(\text{CO})_2\text{I}_2(\text{DAM})_2$
52	$[\text{Rh}_2(\mu\text{-CO})(\mu\text{-Cl})\text{Cl}_2(\text{DPM})_2]\text{PF}_6$
53	$[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2]\text{BF}_4 \cdot 1/2 \text{ CH}_2\text{Cl}_2$
54	$[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}_2(\text{DADPM})_2]\text{BF}_4 \cdot 1/2 \text{ CH}_2\text{Cl}_2$

TABLE I (Continued)

Compound number	Compound
55	$[\text{Rh}_2(\underline{\text{i}}\text{-C}_3\text{H}_7\text{NC})_4\text{Cl}_2(\text{DPM})_2](\text{PF}_6)_2$
56	$[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4\text{I}_2(\text{DPM})_2](\text{PF}_6)_2$
57	$[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{BF}_4)_2$
58	$[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4(\text{CH}_3\text{CN})_2(\text{DPM})_2]^{4+}$
59	$[\text{Rh}_2(\underline{\text{i}}\text{-C}_3\text{H}_7\text{NC})_4(\text{SCN})_2(\text{DPM})_2](\text{BF}_4)_2$
60	$[\text{Rh}_2(\underline{\text{i}}\text{-C}_3\text{H}_7\text{NC})_4(\text{CN})_2(\text{DPM})_2](\text{BF}_4)_2$
61	$[\text{Rh}_2(\underline{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4\text{X}_2(\text{DPM})_2](\text{PF}_6)_4$

Abbreviations used in table:

Bridge = $\mu\text{-CN}(\text{CH}_2)_3\text{NC}$

DADPM = $\mu\text{-(C}_6\text{H}_5)_2\text{AsCH}_2\text{P(C}_6\text{H}_5)_2$

DAM = $\mu\text{-(C}_6\text{H}_5)_2\text{AsCH}_2\text{As(C}_6\text{H}_5)_2$

DPM = $\mu\text{-(C}_6\text{H}_5)_2\text{PCH}_2\text{P(C}_6\text{H}_5)_2$

HH = head-to-head isomer

HT = head-to-tail isomer

X = a substituted pyridine

CHAPTER III

PHOTOLYSIS AND HYDROGEN GENERATION INVOLVING BINUCLEAR

RHODIUM TETRAKISISOCYANIDE COMPLEXES

A number of problems are inherent in hydrogen generating systems involving binuclear rhodium complexes such as 5.^{15,16,49,53-56} The primary difficulty with the use of 5 in the production of hydrogen has been reported to be the very low yields obtained during the photolytic processes (4) (page 13) and (5) (page 14). The quantum yield for the overall process (page 13) has been observed to be as low as 0.0216¹⁶ and even 0.004.⁵⁴ Another major problem with hydrogen generation via complexes similar to 5 is that there have been no reports of practical means of reducing the resulting Rh(II) complex (see Equation 2, page 13) back to the original Rh(I) dimer. Therefore, it is of interest to assess the hydrogen generating capability of the tetrakisocyanide complexes such as 3 because of their structural and electronic similarity to 5.

The first indication that binuclear tetrakisocyanide rhodium complexes could possibly be used to catalyze the reduction of aqueous systems occurred during the attempted recrystallization of $[\text{Rh}_2(\text{CH}_3\text{NC})_4(\text{DPM})_2](\text{PF}_6)$, 22.⁶⁵ When the dark blue methyl isocyanide complex, 22, was dissolved in acetone, the solution turned pale yellow immediately and effervescence was observed. The dramatic color change is characteristic of oxidation of dimeric Rh(I) isocyanide complexes to Rh(II) complexes.² It was thought that the effervescence might have resulted from the reduction of water present in the acetone to dihydrogen.

In order to determine whether the tetrakis(isocyanide) complexes do indeed produce hydrogen by the reduction of water, a 25 volume percent solution of water in acetone was added to an evacuated vial containing compound 22 and the resulting solution was frozen at 77K. The gases present at 77K were excited with an arc discharge and spectral analysis of the resulting emission indicated the presence of two characteristic hydrogen lines at 486.1 and 656.3 Å. These hydrogen lines were not seen in a blank system containing only water and acetone when carried through the same procedure. Therefore, compound 22 and probably the other tetrakis(isocyanide) complexes appear to be capable of catalyzing the production of H₂ from water-acetone mixtures.

Even though compounds such as 22 are apparently responsible for H₂ liberation from aqueous media, the outlook for their use in practical energy systems is not good. Fluorescence measurements by Brown⁶⁶ on 23, the *t*-butyl analogue of 22, have shown that the fluorescence lifetime of these compounds is extremely short (<1 ns at 77K). The tetrakis(isocyanide) complexes 3 are bridged at only two points and are likely to be more flexible than those containing four bridging diisocyanide ligands. Therefore, the tetrakis(isocyanide) dimers are more likely to be susceptible to thermal relaxation. This thermal relaxation appears to be very efficient in decreasing the excited state lifetime. While the fluorescence lifetime of the ¹A_{2u} state of 5 is also very short (< 2 ns), 5 also exhibits a longer-lived triplet

state with a lifetime of ca. 8 μ s.^{67,68} Similar long-lived excited states have not been seen in 23.⁶⁶ Since both thermal and radiative relaxation of excited species decreases the efficiency of photochemical processes,⁶⁹ the quantum yields for the tetrakisocyanide rhodium dimers are expected to be quite low.

In spite of the fact that the tetrakisocyanide complexes 3 appear to have no practical application in the photolytic generation of hydrogen, investigations of the photochemical behavior of these compounds is of interest in light of the recent general interest in organometallic photochemistry.⁷⁰

Purple solutions of the tetrakisocyanide complexes 3 in CH_2Cl_2 or CH_3CN generally change to pale yellow solutions over a period of one to several hours. This transformation appears to be photoinduced or at least photoassisted as shown in Figure 3 for $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 23. Curve 1 in Figure 3 is the UV-Vis absorption spectrum of a 5.0×10^{-5} M solution of 23 in CH_2Cl_2 after sitting in the dark for 4 hours. The solvent was thoroughly deoxygenated with argon. Curve 2 (Figure 3) is the absorption spectrum of a solution identical to the one giving rise to curve 2 (Figure 3) except this solution was photolyzed for 4 hours at 520 nm by means of a xenon arc lamp fitted with a 520 nm bandpass filter. It is evident that the concentration of the absorbing Rh(I) dimer in the photolyzed solution is less than that of the solution that was kept in

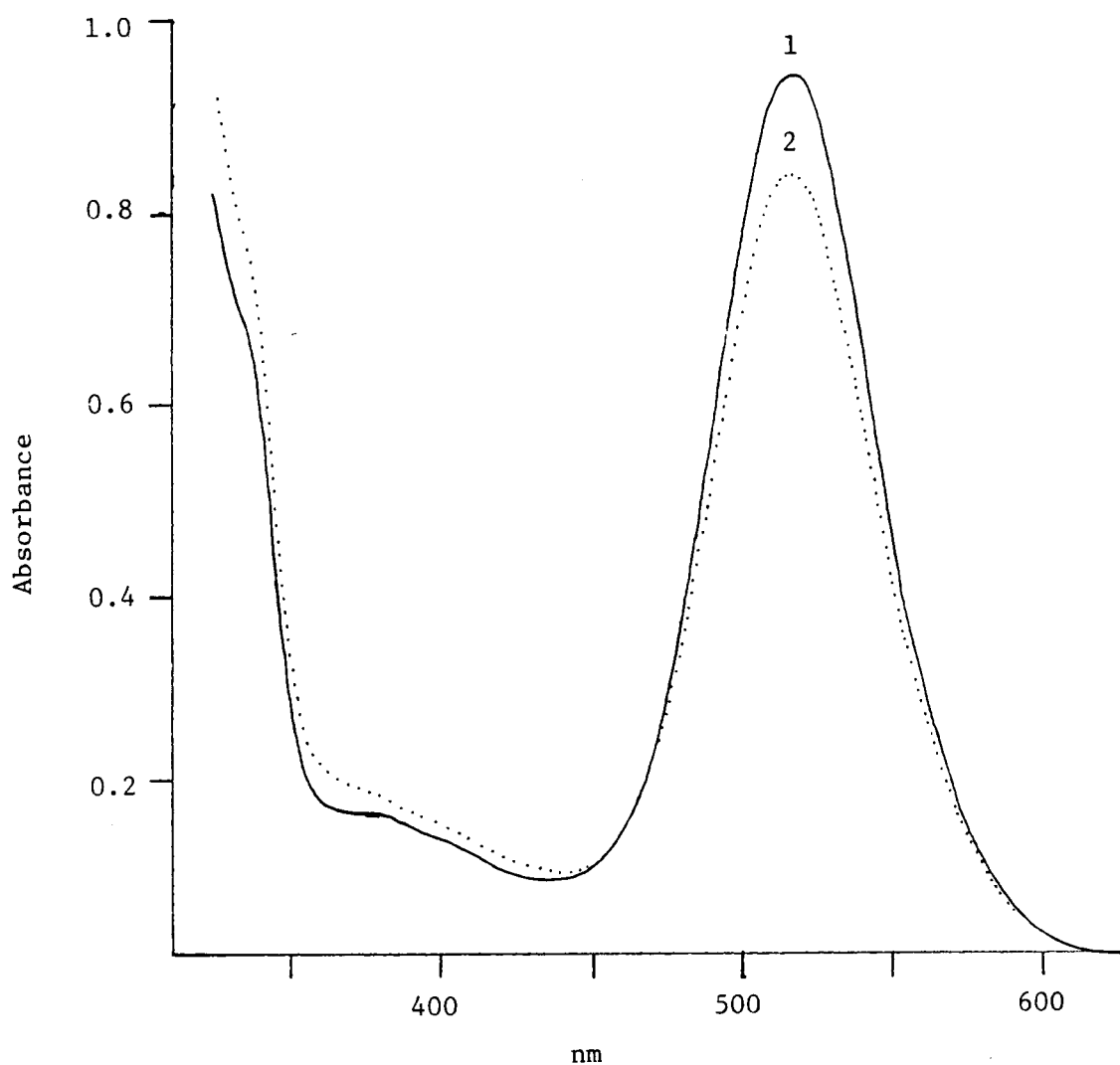


Figure 3. UV-Vis absorption spectra of $5 \times 10^{-5} \text{ M}$ $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 23, in CH_3Cl_2 . Curve 1: spectrum of 23 after sitting in the dark 4 hr. Curve 2: spectrum of 23 after photolysis at 520 nm for 4 h.

the dark. The difference spectrum between the solution kept in the dark and the photolyzed solution is shown in Figure 4. The difference spectrum shows a peak appearing at approximately 465 nm. The decrease in absorbance at 520 nm is also evident in the difference spectrum. The changes depicted in Figure 4 are characteristic of oxidation of rhodium(I) dimers to rhodium(II) dimers.²

The transformation of the tetrakisocyanide complexes indicated by Figures 3 and 4 is much more rapid when oxygen is present. Curve 1 in Figure 5 is the absorption spectrum of a 4.3×10^{-5} M solution of 23 containing oxygen but kept in the dark, whereas Curve 2 is the absorption spectrum of an identical solution of 23 containing oxygen but photolyzed at 520 nm. After only 1.5 hours of photolysis, the original complex had essentially disappeared (Curve 2, Figure 5). In contrast, for the solution that was kept in the dark for 1.5 hr, the concentration was only reduced to approximately 2.6×10^{-5} M. The difference in reaction rate between the photolyzed and nonphotolyzed solutions is further illustrated in Figure 6 for a 4.4×10^{-5} M solution of 23 in oxygenated CH_2Cl_2 . The system was photolyzed at 520 nm for 20 minutes between spectral runs 1-2, 3-4, and 5-6, and the solution was kept in the dark for 20 minutes between runs 2-3 and 4-5. The rate of decrease of the absorbance was markedly reduced in the absence of light but then increased to its former rate when the system was again photolyzed (Table II). Since the reaction occurs both in photolyzed and nonphotolyzed cases, but is much faster during

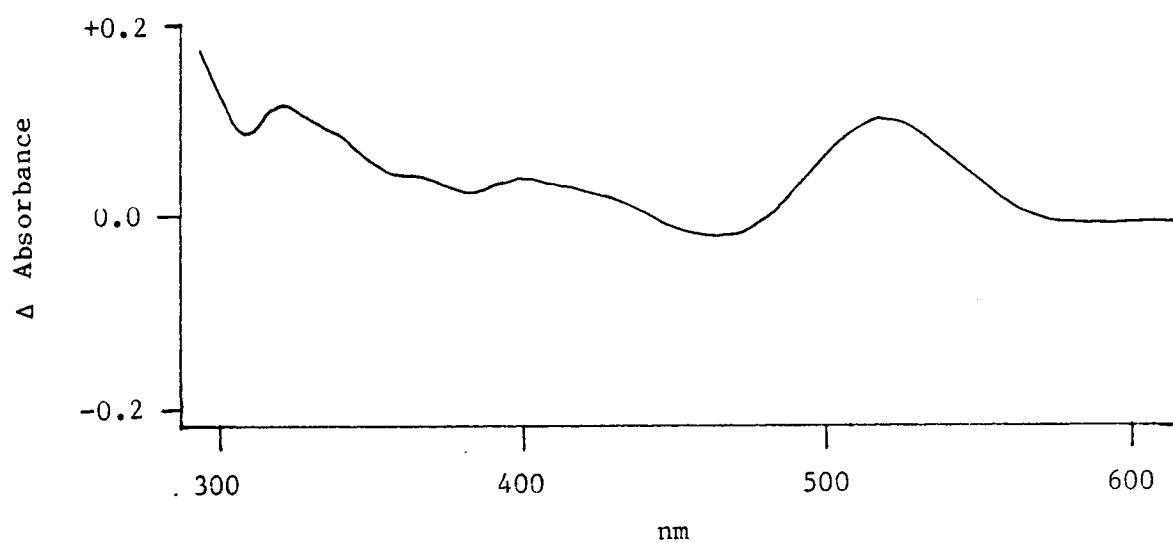


Figure 4. UV-Vis difference spectrum between curves 1 and 2 of Figure 3.

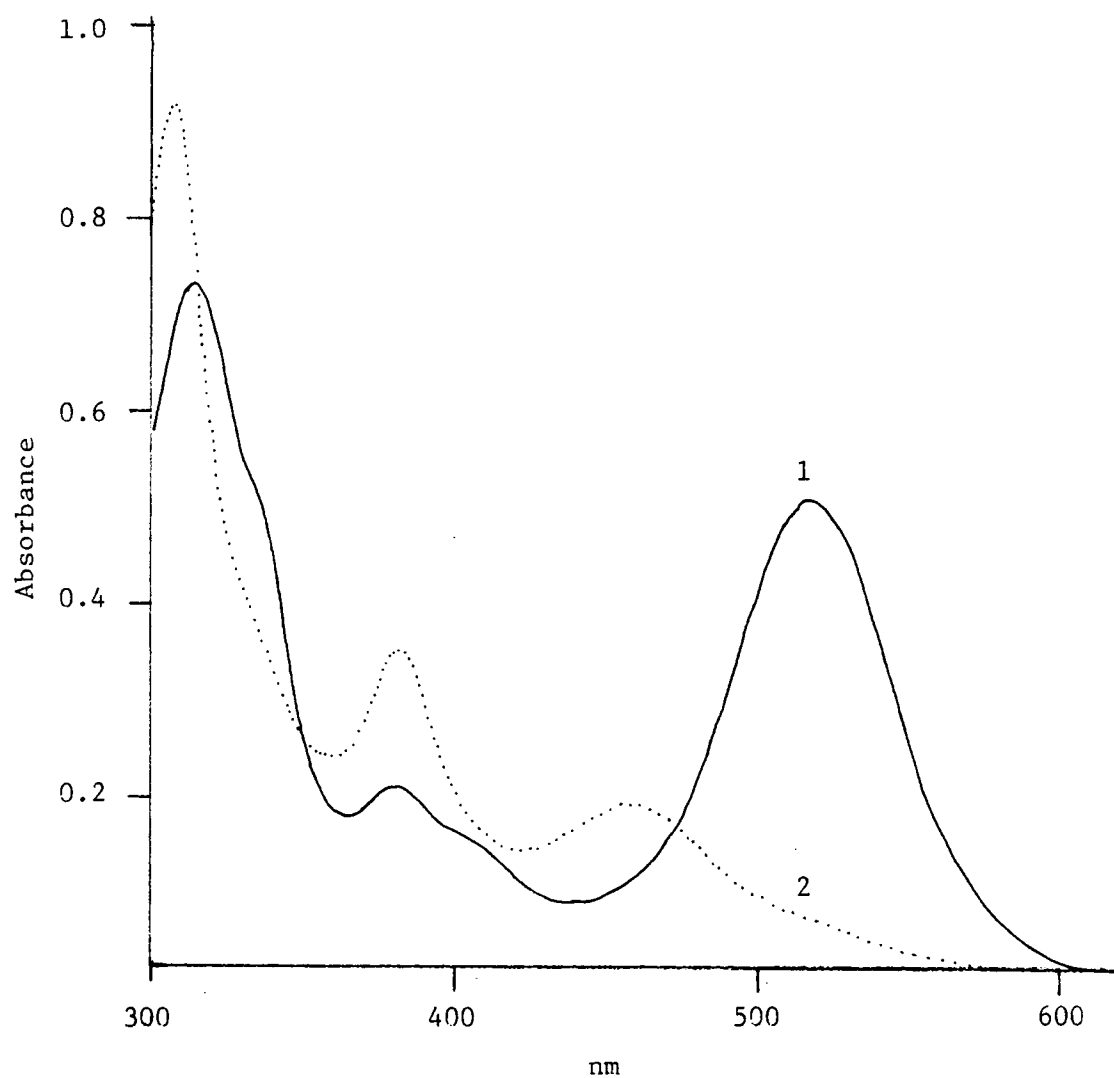


Figure 5. UV-Vis spectra of $4.5 \times 10^{-5} \text{ M}$ $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in oxygenated CH_2Cl_2 . Curve 1: solution kept in dark; curve 2: solution photolyzed at 520 nm for 1.5 h.

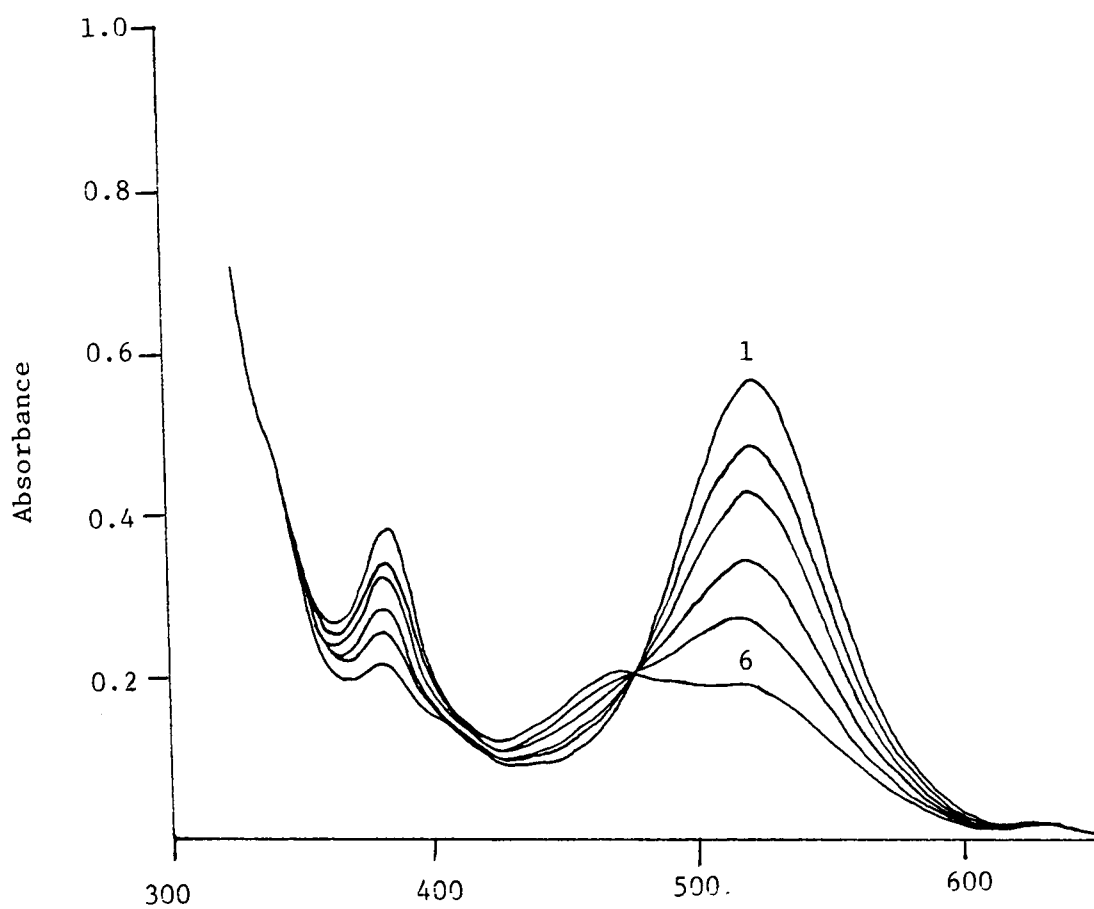


Figure 6. UV-Vis spectrum of $4.3 \times 10^{-5} \text{ M}$ $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 . Curves 1, 3, and 5 were photolyzed at 520 nm for 20 min. Curves 2 and 3 were kept in the dark for 20 min.

TABLE II
CHANGE OF ABSORBANCE WITH TIME FOR $4.4 \times 10^{-5} \text{ M}$
 $[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ IN
 OXYGENATED CH_2Cl_2

Run ^a	Absorbance, A	ΔA^b	Condition
1	0.569	0.079	Photolyzed
2	0.490	0.060	Dark
3	0.430	0.082	Photolyzed
4	0.348	0.069	Dark
5	0.279	0.084	Photolyzed
6	0.195	-	-

^aAll runs were 20 minutes apart.

^b ΔA is the absorbance difference between a given run and the following run.

photolysis, it is likely that a photoassisted thermal reaction involving 23 and oxygen is occurring.

The work of Gray *et al.*⁶⁷ has demonstrated that positive metal centers are capable of halide abstraction from halocarbon solvents. Therefore, if the reaction between 23 and oxygen involves oxidation of the rhodium complex, it may be possible for the resulting Rhodium(II) species to abstract a chloride ion from the CH_2Cl_2 solvent to achieve the preferred coordination number. The resulting complex might be of the form $[\text{Rh}_2(\text{RNC})_4\text{Cl}_2(\text{DPM})_2](\text{PF}_6)_2$, 24. An IR spectrum of the product, isolated from the photolyzed oxygenated CH_2Cl_2 solution of $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 25, exhibited an isocyanide stretch at 2192 cm^{-1} . This represents a $20\text{--}40\text{ cm}^{-1}$ increase in the isocyanide stretching frequency over that of the original complex [$\nu(\text{NC}) = 2150, 2172\text{ cm}^{-1}$]. This shift is consistent with the transformation from Rhodium(I) to Rhodium(II) isocyanide complexes. However, an elemental analysis of the photolysis product indicated that only 35% of the chlorine expected for 24 was present. A similar photolysis of $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{BF}_4)_2$, 26, yielded a product that contained only 13% of the chlorine required for 24.

Since the binuclear rhodium complex 5 has been shown to coordinate to the chloride ion when oxidized in the presence of Cl^- ,^{16,54,71} the compound $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 27, was photolyzed in oxygenated CH_3CN containing excess LiCl . Elemental analysis of the resulting yellow solid indicated that the chlorine

content was higher while the phosphorus content was lower than that expected for the n-butyl isomer of 24.

While it is evident that some process involving visible light and oxygen is responsible for the oxidation of the tetrakisocyanide complexes 3 in both CH_2Cl_2 and CH_3CN , it has not been possible to characterize the oxidation products. In fact, it is likely that the overall reaction leads to an uncharacterizable mixture of products. Although the complexes corresponding to 24 may indeed be some of the photolysis products, they are certainly not the primary products. It is possible that the photolysis process involves the inclusion of oxygen rather than or in addition to chlorine into the rhodium complex.

CHAPTER IV

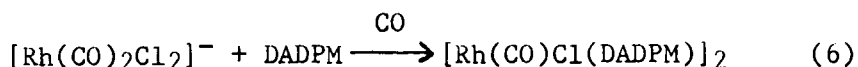
STRUCTURE AND PROPERTIES OF BINUCLEAR RHODIUM COMPLEXES CONTAINING HALIDE AND CARBON MONOXIDE LIGANDS

While 1 and 2 have been shown to be isostructural,^{1,4} investigations of their derivatives containing small bridging species such as CO and Cl have uncovered some interesting cases where the structures and stabilities of the DPM and DAM bridged systems are different.^{3,39} These differences are probably due to the different rhodium-rhodium separations of 1 and 2 and their derivatives⁷²⁻⁷⁷ since the larger bite of DAM requires a larger metal-metal separation than does DPM.^{3,4,35,57}

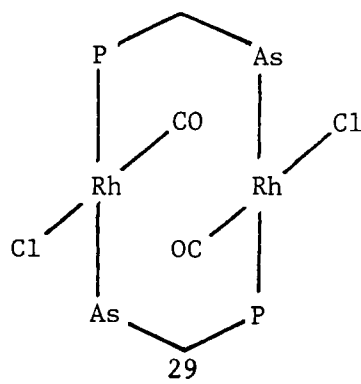
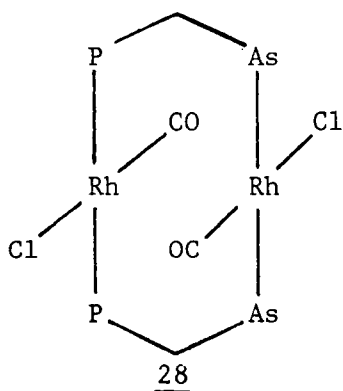
The differences displayed by 1, 2, and their derivatives made the investigation of the compounds of the unsymmetrical ligand $(C_6H_5)_2AsCH_2P(C_6H_5)_2$, (diphenylarsino)(diphenylphosphinomethane, DADPM, of interest. Since the relative bite sizes of DAM and DPM are governed by the different sizes of the arsenic and phosphorus atoms, respectively, it is expected that the bite of DADPM will be between that of DAM and that of DPM because of the presence of both an arsenic atom and a phosphorus atom in the unsymmetrical ligand. It is then expected that the metal-metal distances in DADPM complexes will be intermediate between the corresponding distances in the analogous complexes of 1 and 2. Therefore, it is of interest to compare the structures and stabilities of $[Rh(CO)Cl(DADPM)]_2$ and its derivatives with those of DAM and DPM analogues. Such a comparison should determine whether the DADPM complexes exhibit a behavior similar to either DAM

or DPM complexes, or whether they exhibit a unique behavior, intermediate between that of the DAM analogues and that of the DPM analogues.

The orange product, $[\text{Rh}(\text{CO})\text{Cl}(\text{DADPM})]_2$, obtained by the reaction illustrated by equation 6 is considered to have the CO and Cl ligands on different metal centers in a trans arrangement as is found for 1 and 2. Unlike 1 or 2, the DADPM complex can occur such that the



DADPM ligands are in either the head-to-head arrangement of structure 28 in which both phosphorus atoms are bonded to the same rhodium atom, or the head-to-tail arrangement of structure 29 in which the phosphorus atoms are bound to different rhodium atoms. Both 28 and 29 are shown without a formal metal-metal bond by analogy to 1 and 2.^{1,4}



The lack of a formal metal-metal bond in 28 or 29 is corroborated by the simplicity of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the complex, which displays a simple AX pattern, a simple doublet at 27.3 ppm with $^1J(\text{Rh-P}) = 149 \text{ Hz}$ (Table III). If a formal rhodium-rhodium bond were

TABLE III

 $^{31}\text{P}\{^1\text{H}\}$ NMR SPECTRAL DATA FOR SELECTED COMPOUNDS CONTAINING DADPM

Number	Compound	δ^a	$^1J(\text{Rh-P})^b$
29	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DADPM})_2$	27.3	149
32	$\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-Cl})(\text{DADPM})_2$	27.6	142
35	$\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DADPM})_2$	27.0	146
46	$[\text{Rh}_2(\underline{i}\text{-C}_3\text{H}_7\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$	25.7	144
47	$[\text{Rh}_2(\text{C}_6\text{H}_{11}\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$	25.7	144
48	$[\text{Rh}_2(\text{t-C}_4\text{H}_7\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$	25.5	141

^aChemical shifts were measured in CD_2Cl_2 with respect to 85% H_3PO_4 .^bCoupling constants ± 0.6 Hz.

present, one would expect the NMR spectrum to exhibit an A_2XY pattern for 28 and an $AA'XX'$ pattern for 29. Under these conditions the two isomers could be distinguished by $^{31}\text{P}\{\text{H}\}$ NMR. The unsymmetrical complex 8 investigated by Balch *et al.*^{26,27} contains a formal metal-metal bond and displays a $^{31}\text{P}\{\text{H}\}$ NMR spectrum with an $AA'XX'$ pattern.²⁷ However, in that case the formal rhodium-rhodium bond results from the presence of a bridging CO ligand. Since long range coupling is not observed for $[\text{Rh}(\text{CO})\text{Cl}(\text{DADPM})]_2$, $^{31}\text{P}\{\text{H}\}$ NMR spectroscopy cannot be used to differentiate between isomers 28 and 29.

The IR spectrum of 28 is expected to exhibit two CO stretching frequencies at approximately 1971 cm^{-1} and 1962 cm^{-1} . The first CO frequency is for a CO ligand in the same environment as those in complex 1 and the second CO frequency is for a CO ligand in the same environment as those in complex 2. The IR spectrum of 29 is expected to exhibit a single $\nu(\text{CO})$ located between the corresponding frequencies of 1 and 2. The IR spectrum of *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{DADPM})]_2$ shows a single CO stretching frequency at 1967 cm^{-1} . The band is approximately centered between the carbonyl absorption bands for 1 and 2 (Figure 7). The IR data are therefore consistent with the head-to-tail arrangement of 29 as the structure of $[\text{Rh}(\text{CO})\text{Cl}(\text{DADPM})]_2$. However, because of the small differences in the IR frequencies, further confirmation of the structure was desirable.

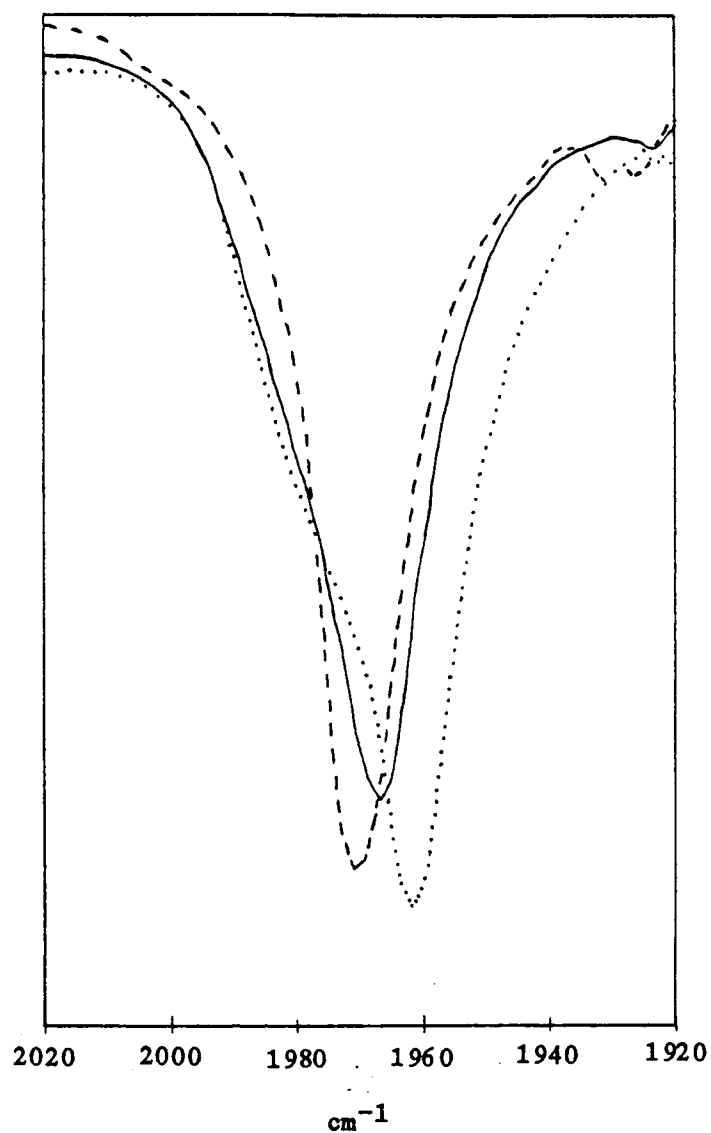


Figure 7. IR spectra (KBr) of $\text{Rh}_2(\text{CO})_2\text{Cl}_2\text{L}_2$. Broken line: L = DPM; solid line: L = DADPM; dotted line: L = DAM.

The ^{13}C NMR spectrum of 28 is expected to exhibit a doublet for the CO ligand coordinated to the arsenic-bonded rhodium atom and a doublet-of-triplets for the CO ligand coordinated to the phosphorus-bonded rhodium atom. These patterns are those expected in the absence of long range rhodium-carbon coupling. On the basis of the ^{31}P ^1H NMR data, such coupling is not expected. Under similar conditions the ^{13}C NMR spectrum of 29 is expected to show a doublet-of-doublets. The actual ^{13}C NMR spectrum of $[\text{Rh}(\text{CO})\text{Cl}(\text{DADPM})]_2$ appears as a doublet-of-doublets (Figure 8) at 188 ppm (from Me_4Si) with $^1J(\text{Rh}-\text{C}) = 73$ Hz and $^2J(\text{P}-\text{C}) = 14$ Hz. The two-bond phosphorus-carbon coupling constant of 14 Hz is also seen in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of ^{13}CO enriched $[\text{Rh}(\text{CO})\text{Cl}(\text{DADPM})]_2$. The phosphorus resonance appears as the expected doublet-of-doublets.

Although the IR and NMR spectra of the compound isolated during our investigation are consistent with structure 29 for $[\text{Rh}(\text{CO})\text{Cl}(\text{DADPM})]_2$, Balch⁷⁸ has more recently isolated a mixture of isomers 28 and 29 upon preparation of $[\text{Rh}(\text{CO})\text{Cl}(\text{DADPM})]_2$ by a procedure reported by Mague and Mitchener.¹ Balch has indicated that the relative abundances of 28 and 29 vary from one synthesis to another with 29 being the more abundant in each synthesis. It may be of interest to note that of the two reported possible methods of preparation,¹ one involves the addition of the bridging arsine or phosphine to $[\text{Rh}(\text{CO})\text{Cl}]_2$ while the other involves addition of the ligand to $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ that has been refluxed under CO. It is possible that slight differences in

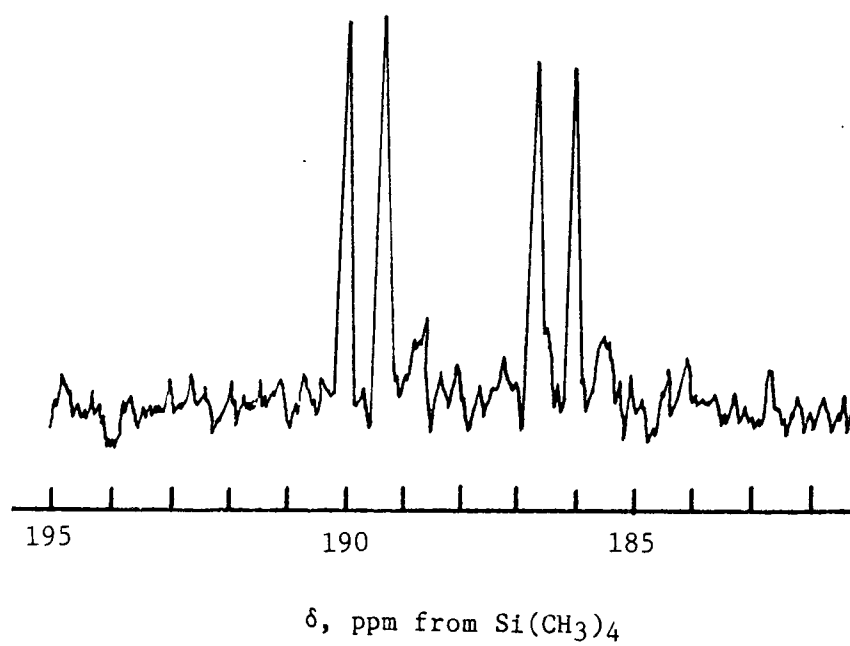
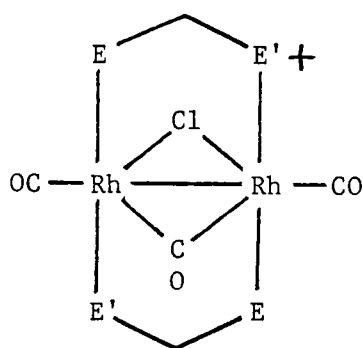


Figure 8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Rh}_2(^{13}\text{CO})_2(\text{DADPM})_2$.

preparation procedures may account for the presence of a mixture of isomers, perhaps for kinetic reasons. We have not found conclusive evidence for the presence of 28 together with 29; however, it may be possible that 28 is indeed present, but in a concentration too low to allow its detection under the conditions used in this investigation.

It is of interest to compare the stabilities of derivatives of 29 in cases where the analogous derivatives of 1 and 2 display markedly different stabilities. If equimolar amounts of DPM and ammonium hexafluorophosphate are added to an ethanol solution of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ under carbon monoxide, the resulting complex is reported^{30,33} to contain the cation of structure 30 and appears to be stable indefinitely both in solution and in the solid phase. However, if nitrogen is bubbled through a solution containing 30, the bridging carbonyl group is readily lost to form the dicarbonyl complex ion 33.³⁹

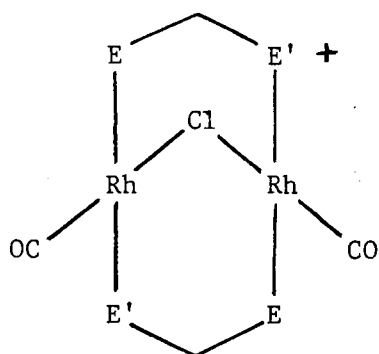


30; E = E' = P

31; E = E' = As

32; E = P, E' = As

This behavior is in contrast to the hexafluorophosphate salt of the DAM analogue, which probably exists as the tricarbonyl species 31 in solution, but demonstrates a strong tendency to lose the bridging carbonyl group to form 34 immediately upon isolation as a solid.



33; E = E' = P

34; E = E' = As

35; E = P, E' = AS

The stability of the hexafluorophosphate salt of 31 in the solid phase could be kinetic rather than thermodynamic in nature since Mague and DeVries³ have noted the presence of crystalline 31 in some preparations of the dicarbonyl compound $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DAM})_2]\text{PF}_6$, 34, and not in others. In the cases where the tricarbonyl compound 31 was seen, loss of the bridging carbonyl group occurred overnight. However, structure 31 can be obtained as a stable solid when isolated as the tetraphenylborate salt.³⁹ Apparently the difference in stability of the hexafluorophosphate and tetraphenylborate salts of 31 is due to packing phenomena that occur in the solid, with the larger anion allowing 31 to retain the bridging carbonyl.³

When equimolar quantities of DADPM and ammonium hexafluorophosphate are added to ethanol solutions of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ under carbon monoxide, orange crystals are produced that exhibit three IR absorption frequencies at 1981, 1967, and 1843 cm^{-1} if the IR spectrum is taken immediately after isolation. These bands are indicative of the presence of at least two terminal and one bridging carbonyl groups; therefore the resulting complex is formulated as

$[\text{Rh}_2(\mu\text{-CO})(\text{CO}_2)(\mu\text{-Cl})(\text{DADPM})_2]\text{PF}_6$, 32. The bridging chloride and formal metal-metal bond are postulated on the basis of the electron count of the rhodium and by analogy to the corresponding DPM complex 30.^{30,33} The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 32 under CO exhibits only a simple doublet (Table II, page 53) rather than a second order pattern. The absence of the expected second order spectrum at ca. 298K is consistent with a reduced rhodium-rhodium interaction resulting from rapid CO exchange as observed in 30 by Cowie and coworkers.³⁰

It was determined that 30 is an AA'A''A'''XX' spin system at 223K.³⁰ While the DADPM monocarbonyl complex is readily isolable as 32, IR data indicate the loss of the 1843 cm^{-1} band from the solid upon standing overnight (Figure 9). The product resulting from the loss of the bridging CO has been formulated as 35. It is of interest to note that the behavior of 32 is intermediate between that of 30, which is stable to loss of CO in the solid state, and 31, which cannot be isolated as the corresponding hexafluorophosphate salt. In the case of the diarsine derivative, only 34 can be isolated.

Since 32 displayed behavior intermediate between the more stable DPM and the less stable DAM analogues, it was of interest to determine the behavior of other derivatives of 29 in cases where the corresponding derivatives of 1 and 2 were again different. Addition of Br^- to 1 using NaBr is reported to produce the species $[\text{Rh}_2(\mu\text{-CO})(\text{CO})\text{Br}(\text{DPM})_2]\text{Br}$ which readily reacts with CO to produce a complex formulated⁴ as 36, the bromo analogue of the cation 30. This

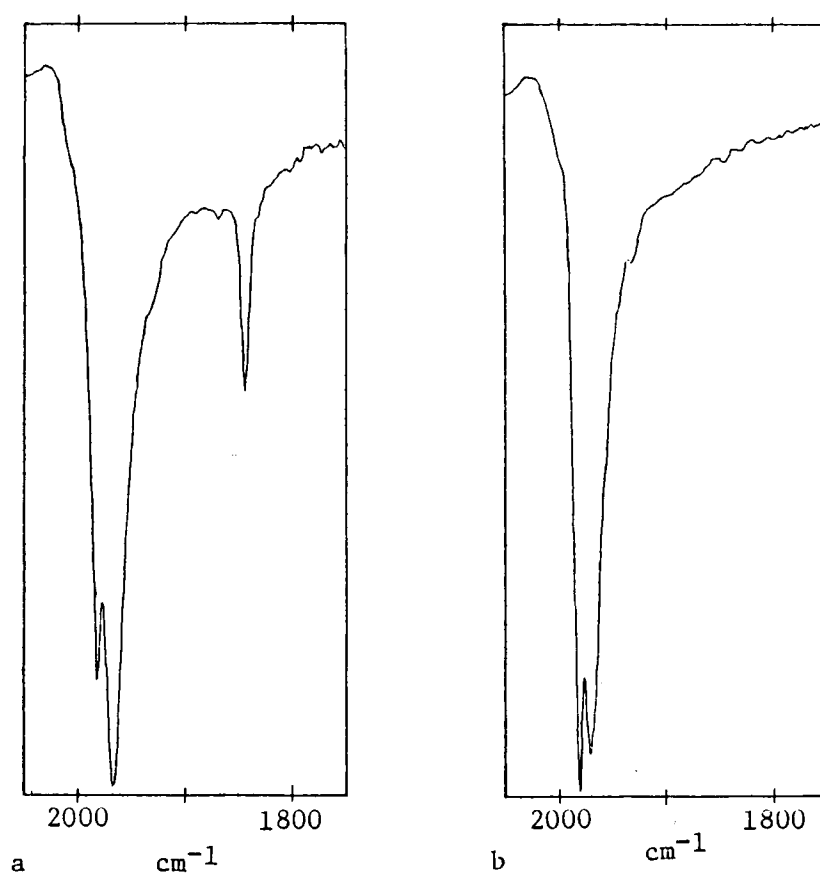
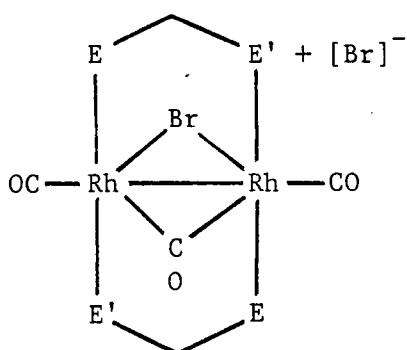


Figure 9. IR spectra (Nujol) of $[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2\text{Cl}(\text{DADPM})_2]\text{PF}_6$.
(a) Immediately upon isolation; (b) after standing overnight.

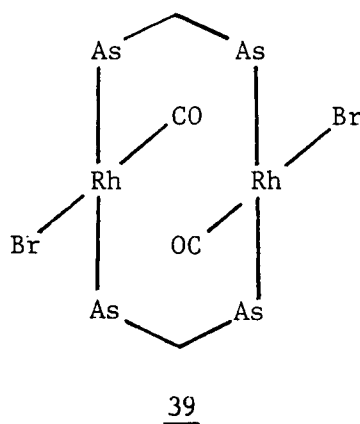


36; E = E' = P

37; E = E' = As

38; E = P, E' = As

behavior is in contrast to that of the DAM compound 2,^{1,64} which upon addition of Br^- does not give a compound of structure 37, but instead gives compound 39, which also results from the addition of equimolar amounts of DAM and $[\text{Rh}(\text{CO})_2\text{Br}_2]^-$. Both 36 and 39 are stable toward



CO loss in the solid phase. Addition of DADPM to $[\text{Rh}(\text{CO})_2\text{Br}_2]^-$ produces a yellow solid that exhibits IR absorption bands at 1998, 1952 and 1869 cm^{-1} (Figure 10). The two higher energy bands are indicative of the presence of at least two terminal carbon monoxide ligands while the band at 1869 cm^{-1} is assigned to a bridging carbon monoxide. Therefore, the DADPM complex is formulated as

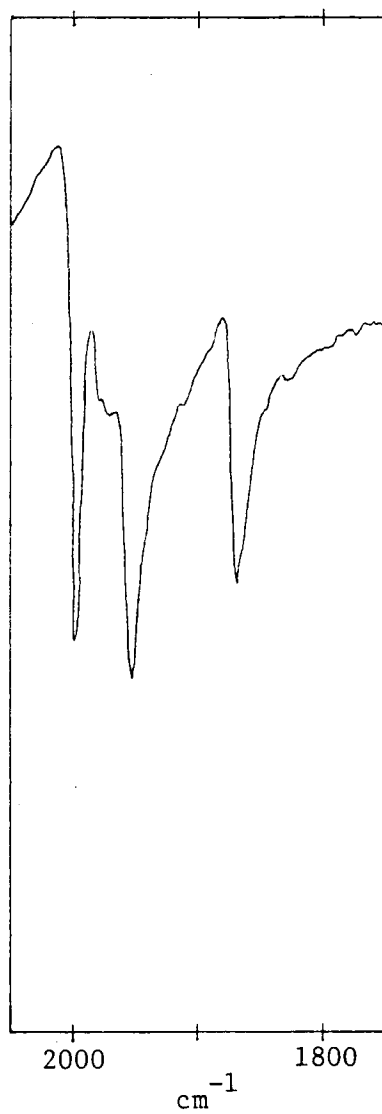
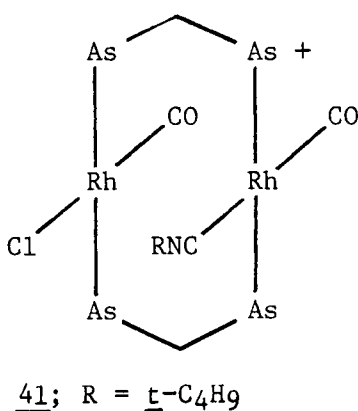
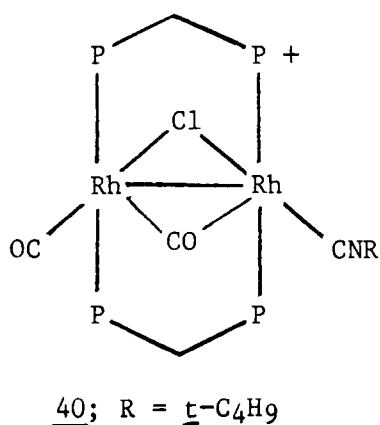


Figure 10. IR spectrum (Nujol) of $\text{Rh}_2\text{Br}_2(\mu\text{-CO})(\text{CO})_2(\text{DADPM})_2$.

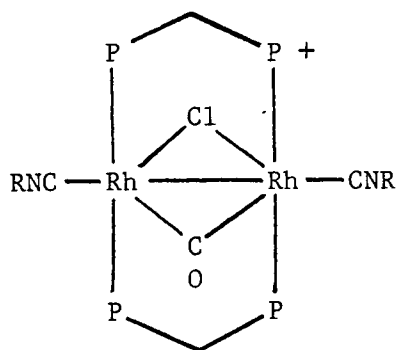
$[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-Br})(\text{DADPM})_2]\text{Br}$, 38, analogous to 36, the bromo analogue of 1 rather than 2.

Another interesting case of contrasting behaviors of the DAM and DPM systems arises from their mono- and diisocyanide derivatives. Treatment of 33 with one equivalent of $\underline{t}\text{-C}_4\text{H}_9\text{NC}$ results in a compound formulated as 40.³ Under identical conditions, complex 34 leads to a compound of structure 41.³

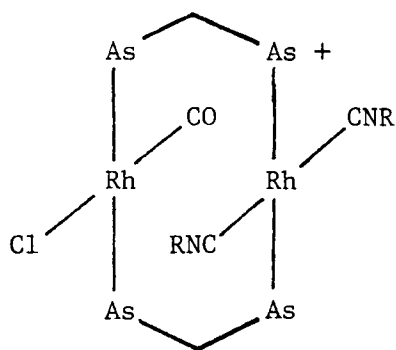


Addition of two equivalents of $\underline{t}\text{-C}_4\text{H}_9\text{NC}$ to 33 results in the addition of an isocyanide ligand to each rhodium, the loss of one carbon monoxide ligand, and the formation of a bridging carbon monoxide to give structure 42. Addition of two equivalents of $\underline{t}\text{-C}_4\text{H}_9\text{NC}$ to 34 results in the binding of the isocyanide groups to the same metal center to give complex 43.³

Addition of one equivalent of $\underline{t}\text{-C}_4\text{H}_9\text{NC}$ to 35 produces an orange solid that exhibits IR absorption bands at 1954 and 2005 cm^{-1} , indicative of at least two terminal carbon monoxide ligands and a band at 2209 cm^{-1} that has been assigned to a terminal isocyanide ligand.

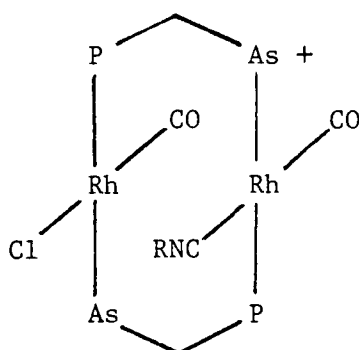


42; R = t-C₄H₉



43; R = t-C₄H₉

On the basis of these data, and the absence of IR bands indicative of bridging ligands, the complex is formulated as 44. By analogy with 41, the carbon monoxide ligands are presumed to be in a cis configuration since such a structure would require a minimum amount of



44; R = t-C₄H₉

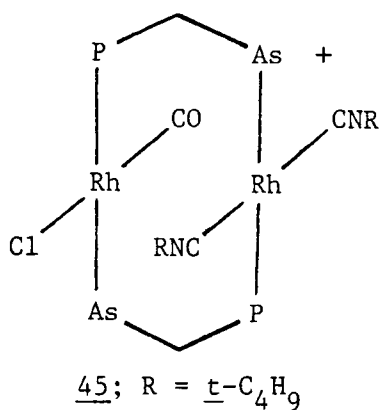
rearrangement of the chloro-bridged precursor 35 and the chloride ligand is assumed to be terminal since that would result in a square planar arrangement and a formal electron count of 16 for each rhodium atom (a chloro-bridged species would result in an electron count of 16 for one metal atom and 18 for the other).³ The two carbon monoxide ligands are most likely coordinated to different metal atoms since the

51 cm^{-1} difference in the carbon monoxide stretching frequencies indicates different environments for the CO ligands. By analogy to the assignments of the IR bands for 41,³ the lower energy CO stretch (1954 cm^{-1}) is assigned to the carbon monoxide ligand trans to the chloride because that CO ligand is in an environment similar to the carbon monoxide ligands in 29 whose stretching frequency occurs at 1967 cm^{-1} . This assignment is also supported by the fact that isocyanides are better π acceptors than halides;⁷⁹ therefore, the t-C₄H₉NC can better compete with CO for metal π -electron density than can the Cl⁻. Thus, the carbon monoxide ligand trans to the chloride will have the higher CO stretching frequency. The existence of a CO trans to an isocyanide ligand is also consistent with the high CN stretching frequency of 44. Since CO is a better π acceptor than isocyanides,⁷⁹ less π donation from the metal to the RNC ligand occurs when that ligand is trans to a CO than when it is trans to another isocyanide. Therefore, the NC stretch occurs at a much higher frequency in 44 than in 45 (Vide infra).

Addition of two equivalents of t-butylisocyanide to 35 results in a red solid which exhibits an IR absorption band at 1954 cm^{-1} that can be assigned to a terminal carbon monoxide and one at 2120 cm^{-1} that can be assigned to a terminal isocyanide ligand. The resulting complex is therefore formulated as 45. Using an argument similar to the one employed for 44, the carbon monoxide ligand is trans to a chloride due to the close proximity of $\nu(\text{CO})$ for 45 to those of both 29 and 44. The lower value of $\nu(\text{NC})$ for 45 compared to that of 44

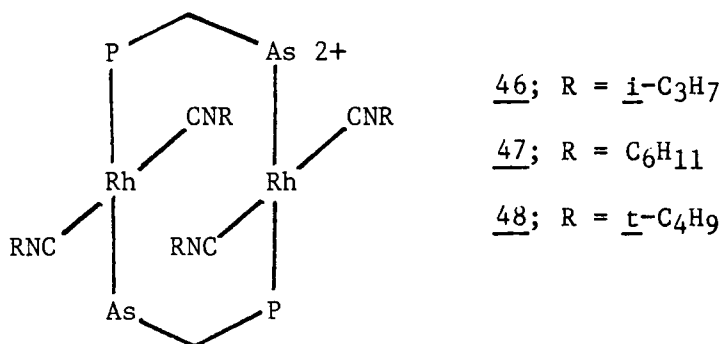
suggests that no isocyanide is trans to carbon monoxide and therefore both RNC groups are most likely coordinated to the same metal center as was found for the DAM complex 43.

Neither 44 nor 45 is stable in deoxygenated CH_2Cl_2 or CH_3CN as demonstrated by rapid changes in their UV-visible spectra (Table II). Therefore, it is not possible to further investigate these compounds by



means of NMR techniques, unless a solvent in which they are stable can be used.

Treatment of complex 29 with four equivalents of i-propyl-, t-butyl-, or c-hexylisocyanide results in a series of tetrakis-isocyanide complexes 46-48. These complexes are formulated



as having the same general structure as the analogous DPM and DAM compounds 3 and 4.^{6,10} Complexes 46-48 display UV-visible and IR spectra similar to 3 and 4,⁵ (Table IV) and also react with oxygen in CH₂Cl₂ or CH₃CN in analogy to the behavior of the DPM complexes (Chapter III). The ³¹P{¹H} NMR spectra of complexes 46-48 are also similar to 29 in that they display no long-range rhodium-phosphorus coupling. The NMR spectra of 46-48 show only simple doublets (Table III, page 59).

It appears that the differences in stability and structure exhibited by the DAM, DPM, and DADPM complexes containing carbon monoxide and halide ligands are primarily due to the differences in the rhodium-rhodium separation imposed by the varying bite sizes of the bridging arsine or phosphine ligands. In the case of the complexes 30-32, the DAM system 31 is much less stable than the DPM compound 30, most likely due to the larger metal-metal separation of 31. It has been found that bridging carbon monoxide is generally less stable and undergoes exchange more readily in DAM complexes than in DPM complexes.^{3,39} Therefore, it is not surprising to find the DADPM complex 32 more stable than 31 but less stable than 30 toward loss of CO since this metal-metal distance in 32 is presumably intermediate between the corresponding distance for 30 and 31.

An additional factor besides the stability of the bridging CO ligand appears to be playing a role in establishing the differences between the bromide complexes as represented by 36-39. While the DAM

system has been observed not as the bromide bridged complex 37 but as the readily made dibromide 39, the DPM and DADPM bromides have been found exclusively as the bridged species 36 and 38 rather than the bromo analogues of the terminal complexes 1 and 29. The failure of the DAM compound to appear as 37 may be explained on the basis of the inability of the DAM compound to form a stable CO bridge due to a rhodium-rhodium separation that is too large. However, the inability of the DPM and DADPM dibromo compounds to form the bromide derivatives of 1 and 29 (c.f. 33) may be due to the smaller bite sizes of the bridging ligands not allowing the carbon monoxide ligands and the relatively large bromide ion to simultaneously coordinate to the metal center in the DPM and DADPM complexes. So, only the DAM complex with the larger bite can accommodate a structure such as 39 with the larger halides such as bromide or iodine.⁴

In light of the interest expressed recently in the ability of DPM and DAM compounds 1 and 2 to form A-frame complexes that are coordinatively unsaturated and are therefore able to add small molecules, complexes 33,³⁹ 34,³ and 35 may be of general interest. These compounds are also of interest since in addition to displaying A-frame geometries, they also have bridging chloride ligands. This is in contrast with expectations that CO will bridge preferentially to halides in derivatives of 1, 2, and 29. These expectations are based on the fact that CO is a much better π acceptor.³²

TABLE IV

IR AND UV-VIS SPECTRAL DATA FOR SELECTED COMPOUNDS CONTAINING DADPM

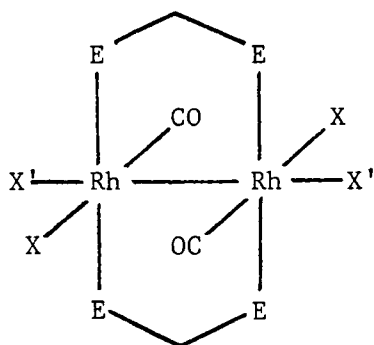
Number	Compound	$\nu(\text{CO}), \text{cm}^{-1}$	$\lambda(\text{CN}), \text{cm}^{-1}$	$\lambda_{\text{max}}, \text{nm} (\epsilon)$
29	$\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DADPM})_2$	1967 (S)		455 (6740), 283 (Sh)(17,300)
32	$\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-Cl})(\text{DADPM})_2$	1981(S), 1967(S), 1843(M)		
35	$\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DADPM})_2$	1981(S), 1965(S)		435 (10,600), 305 (Sh)(12,700)
38	$[\text{Rh}_2\text{Br}(\mu\text{-CO})(\text{CO})_2(\text{DADPM})_2\text{Br}]$	1998(M), 1952(M), 1869(M)		447 (3900), 344 (8270), 290 (Sh)(16,900)
44	$[\text{Rh}_2(\text{CO})_2\text{Cl}(\text{t-C}_4\text{H}_9\text{NC})(\text{DADPM})_2]\text{PF}_6$	2005 (S), 1954 (S)	2209 (M)	443 (5750), ^a 380 (3700), ^b 305 (Sh)(10,200)
45	$[\text{Rh}_2(\text{CO})\text{Cl}(\text{t-C}_4\text{H}_9\text{NC})_2(\text{DADPM})_2](\text{PF}_6)_2$	1954 (S)	2120 (S)	515 (3650), ^a 458 (4860), ^b 383 (3540), 302 (Sh)(12,000)
46	$[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$	2144 (S)		545 (9160), 322 (13,000) 264 (Sh)(13,400)
47	$[\text{Rh}_2(\text{C}_6\text{H}_4\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$		2166 (M), 2137 (S)	548 (1500), 322 (1300) 265 (Sh)(20,600)
48	$[\text{Rh}_2(\text{t-C}_4\text{H}_9\text{NC})_4(\text{DADPM})_2](\text{PF}_6)_2$		2153 (M), 2125 (S)	517 (11,300), 385 (4650), 323 (14,500), 265 (16,300)

^aMolar absorptivity rapidly decreases with time.^bMolar absorptivity rapidly increases with time.

CHAPTER V

ELECTROCHEMISTRY OF BINUCLEAR RHODIUM COMPLEXES CONTAINING ISOCYANIDE AND CARBON MONOXIDE LIGANDS

Investigations of rhodium dimers containing carbon monoxide, halide, and isocyanide ligands have been primarily restricted to their Rh(I) complexes. It is known that the structure and properties of the Rh(I) analogues of 1, 2, and 29 are dependent upon the rhodium-rhodium separation governed by the various bite sizes of the bridging DPM, DAM, or DADPM ligands.^{3,4,29,39} However, a similar dependence of the behavior of Rh(II) derivatives of 1, 2, and 29 upon the bridging ligand has not been demonstrated. The behavior of Rh(II) binuclear complexes containing carbon monoxide and halide ligands is also important in light of the redox behavior displayed by complexes such as 9 during their application as homogeneous catalysts.⁴¹ It appears that the only reported Rh(II) analogues of 1, 2, and 29 are the oxidative addition products of Br₂ or I₂ with 1 or 2 to produce the diamagnetic complexes 49-51.²



49; E = P, X = Cl, X' = I

50; E = As, X = Br, X' = Br

51; E = As, X = Br, X' = I

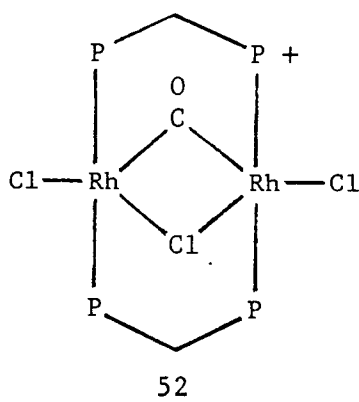
Since very little data exist for Rh(II) derivatives of binuclear halocarbonyl complexes, some aspects of the electrochemical behavior of 1, 2, and 29 have been investigated in this work.

A great deal of interest in the redox properties of binuclear Rh(I) isocyanide complexes has arisen since the investigation of the hydrogen generating capability of compound 5 by Gray and coworkers.^{15,16,49,53-56} The overall hydrogen generating process results in the production of the Rh(II) complex 20^{53,54} by way of the mixed oxidation state oligomer 21^{53,55,56} as shown in Equations (2)-(5) (pages 13 and 14). Complex 20 has been characterized as being identical to the product obtained from oxidative addition of Cl₂ to 5.¹⁵ It is therefore of interest to compare the behavior of tetrakis(isocyanide) binuclear rhodium complexes of type 3 with compound 5 since 3 and 5 are structurally and electronically similar.

A. Electrochemical Behavior of Binuclear Rhodium Complexes Containing Chloride and Carbon Monoxide Ligands

In view of the lack of any reported chloride analogues of the Rh(II) complexes 49-51 and the inability to characterize the oxidative-addition products of 1, 2, or 29 with Cl₂, Tinsley⁶⁴ has investigated the electrochemical behavior of 1 and 2 in CH₂Cl₂ in the presence of excess (C₄H₉)₄NCl. His work demonstrated that a yellow solution of complex 1 exhibits an irreversible oxidation peak at +0.40 V in the presence of excess Cl⁻, and that the controlled potential

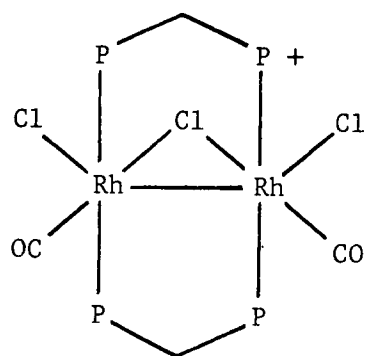
electrolysis at +0.6 V of the system containing 1 results in a two-electron oxidation and produces an orange solution. Tinsley found that after oxidation the original complex could not be regenerated by the reduction of the oxidation product. An orange solid consisting of a mixture of the oxidation product of 1 with $(C_4H_9)_4NPF_6$ was obtained upon stripping off the CH_2Cl_2 after the oxidation. The orange oxidation product exhibited an IR band at 2024 cm^{-1} which was assigned to a single terminal carbon monoxide ligand. The presence of only one carbon monoxide group in the oxidation product is consistent with the inability to regenerate complex 1 after its oxidation. Tinsley's separation of the oxidation product from the supporting electrolyte and the excess $(C_4H_9)_4NCl$ resulted in a green compound that exhibited an IR band at 1802 cm^{-1} which was assigned to a single bridging carbon monoxide ligand. The compound that was isolated has been formulated as $[Rh_2Cl_2(\mu-Cl)(\mu-CO)(DPM)_2]PF_6$, 52.⁶⁴



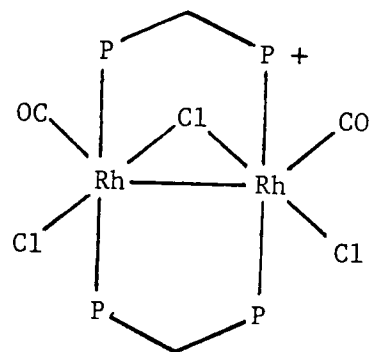
Complex 52 has been formulated as containing a ketonic carbonyl group rather than a conventional bridging carbonyl group (a ketonic

carbonyl is defined as a carbon monoxide ligand bridging two metal atoms that are not bound by a formal metal-metal bond.⁴¹) Only three binuclear complexes (one platinum,⁷⁵ one palladium,^{73,74,80} and one rhodium⁴¹ complex) containing a ketonic carbonyl group have been reported. Even though the $\nu(\text{CO})$ for ketonic carbonyls in Rh(I) complexes is expected to be lower than conventionally bridged carbonyls (ca. 1700 cm^{-1} ,⁴¹ the same region for organic carbonyl groups⁴¹), the $\nu(\text{CO})$ at 1802 cm^{-1} in the IR spectrum of 52, a Rh(II) complex, has been assigned to a ketonic carbonyl group.

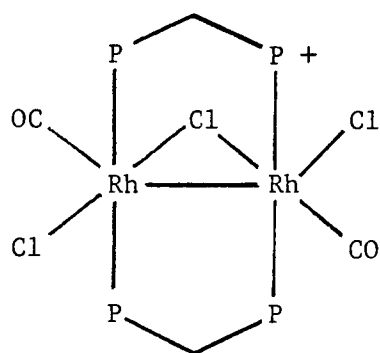
Tinsley⁶⁴ demonstrated that the electrochemical behavior of the DAM-bridged complex 2 in the presence of $(\text{C}_4\text{H}_9)_4\text{NCl}$ differed from that of complex 1 in that a two-electron oxidation of 2 at $+0.73\text{ V}$ resulted in an orange complex that could be reduced back to the original dimer. Isolation of the oxidation product of 2 as the tetrafluoroborate salt resulted in an orange compound that gave IR bands at 1992 and 1982 cm^{-1} which were assigned to two terminal carbon monoxide ligands. Tinsley has formulated the isolated oxidation product as $[\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-Cl})(\text{DPM})_2\text{BF}_4] \cdot 1/2\text{ CH}_2\text{Cl}_2$, 53, based on the IR spectrum and the elemental analysis. Three isomers for compound 53 have been suggested⁶⁴ and are shown in Figure 11. The presence of the bridging chloride ligand has been assumed in order for the electron counts for the two rhodium atoms to be the same.⁶⁴ The most probable structure for 53 is the one in which the two carbon monoxide ligands are trans to one another since that configuration would require the least amount of rearrangement of the original complex upon coordination of the chloride ion.



A



B



C

Figure 11. Three possible isomers for $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})\text{Cl}_2]^- (\text{DPM})_2] \text{BF}_4 \cdot 1/2 \text{CH}_2\text{Cl}_2$.

The difference in the electrochemical behavior between 1 and 2 in the presence of excess chloride ions indicated that a comparison of the electrochemical behavior of the DADPM-bridged complex 29 with that of 1 and 2 would be of interest. Figure 12 shows the voltammogram of 29 in CH_2Cl_2 and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$ with a 10-fold excess of $(\text{C}_4\text{H}_9)_4\text{NCl}$ present. Sweeping through the oxidation peak at +0.55 V produces a species that undergoes reduction at about -0.5 V. This behavior is similar to that of 2 but different from that of 1.⁶⁴ If 29 is oxidized at +0.65 V by controlled potential electrolysis a two-electron transfer occurs that produces a species whose voltammogram is shown in Figure 12b. Reduction of the oxidation product of 29 regenerates the oxidation peak seen in the original rhodium(I) complex 29 (see Figure 12b). Isolation of the oxidation product yielded an orange complex that exhibited IR bands at 1996 and 1980 cm^{-1} which are assigned to two terminal carbon monoxide groups. Analytical data for the oxidation product are consistent with the formulation of the complex as $[\text{Rh}_2(\text{CO})_2\text{Cl}_3(\text{DADPM})_2\cdot\text{BF}_4]\cdot 1/2 \text{CH}_2\text{Cl}_2$, 54. By analogy to the arguments presented by Tinsley⁶⁴ for compound 53, complex 54 is assigned structure C in Figure 11.

B. Electrochemical Behavior of Tetrakisocyanide Complexes in Dichloromethane

In light of the interest expressed in the behavior of Gray's hydrogen generating complex 5 and its chlorine oxidative addition product 20, an investigation of possible analogous redox behavior of

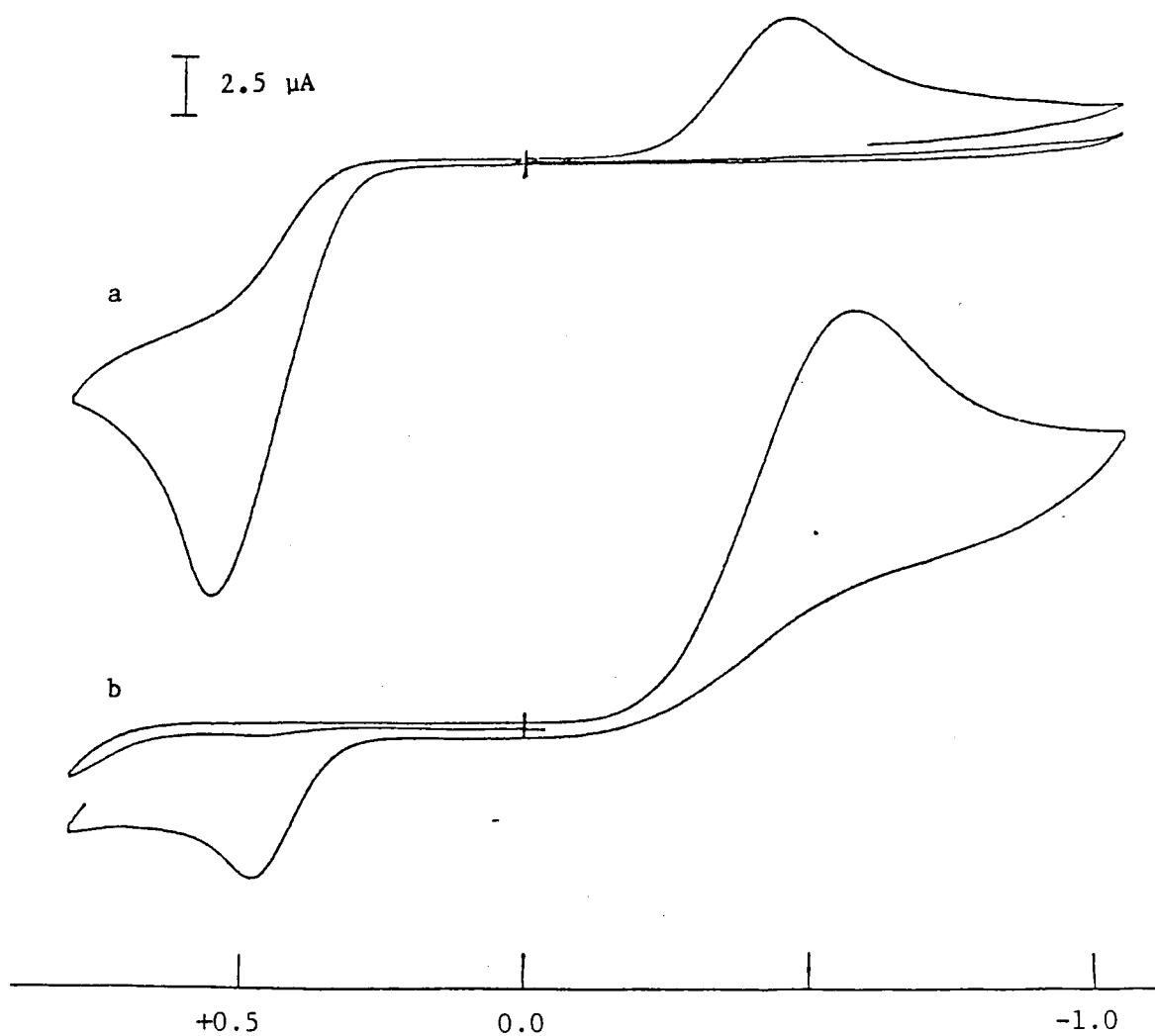
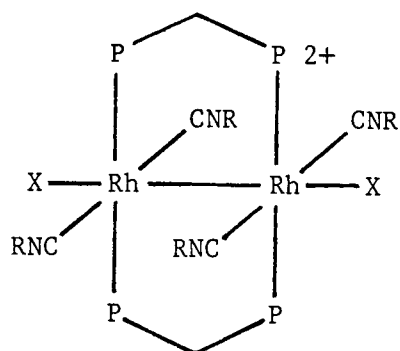


Figure 12. Cyclic voltammograms of (a) $10^{-3} \text{ M Rh}_2(\text{CO})_2\text{Cl}_2$ (DADPM) $_2$ in CH_3CN , $0.1 \text{ M (C}_4\text{H}_9)_4\text{NBF}_4$, and $2 \times 10^{-3} \text{ M (C}_4\text{H}_9)_4\text{NCl}$ and (b) the same system as Figure 12a oxidized at +0.65 V.

$[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 25, to form the binuclear Rh(II) chloride complex 55 was initiated.



55; $\text{R} = \text{i-C}_3\text{H}_7$; $\text{X} = \text{Cl}$

56; $\text{R} = \text{n-C}_4\text{H}_9$; $\text{X} = \text{I}$

Although 55 and its DAM analogue obtained by the direct addition of I_2 or Br_2 to a rhodium isocyanide dimer bridged by DPM or DAM, respectively, have been reported,^{2,5} attempts in this work to produce 55 by the direct addition of Cl_2 to 25 have not been successful. Additional attempts to make 55 by either chemical oxidation by NOPF_6 or photochemical oxidation of 25 in the presence of chloride ions apparently results in an uncharacterizable mixture of products. Because of the inability to produce 55 by chemical means, the possibility of generating this complex by electrochemical methods was considered since such techniques allow a much greater degree of control of the oxidation potential. Therefore, the electrochemical behavior of some tetrakisocyanide rhodium dimers has been investigated.

Figure 13 shows the cyclic voltammogram of $\text{Rh}_2[(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 25, in CH_2Cl_2 and 0.1 M $\text{C}_4\text{H}_9\text{NPF}_6$ and is representative of the electrochemical behavior of the binuclear

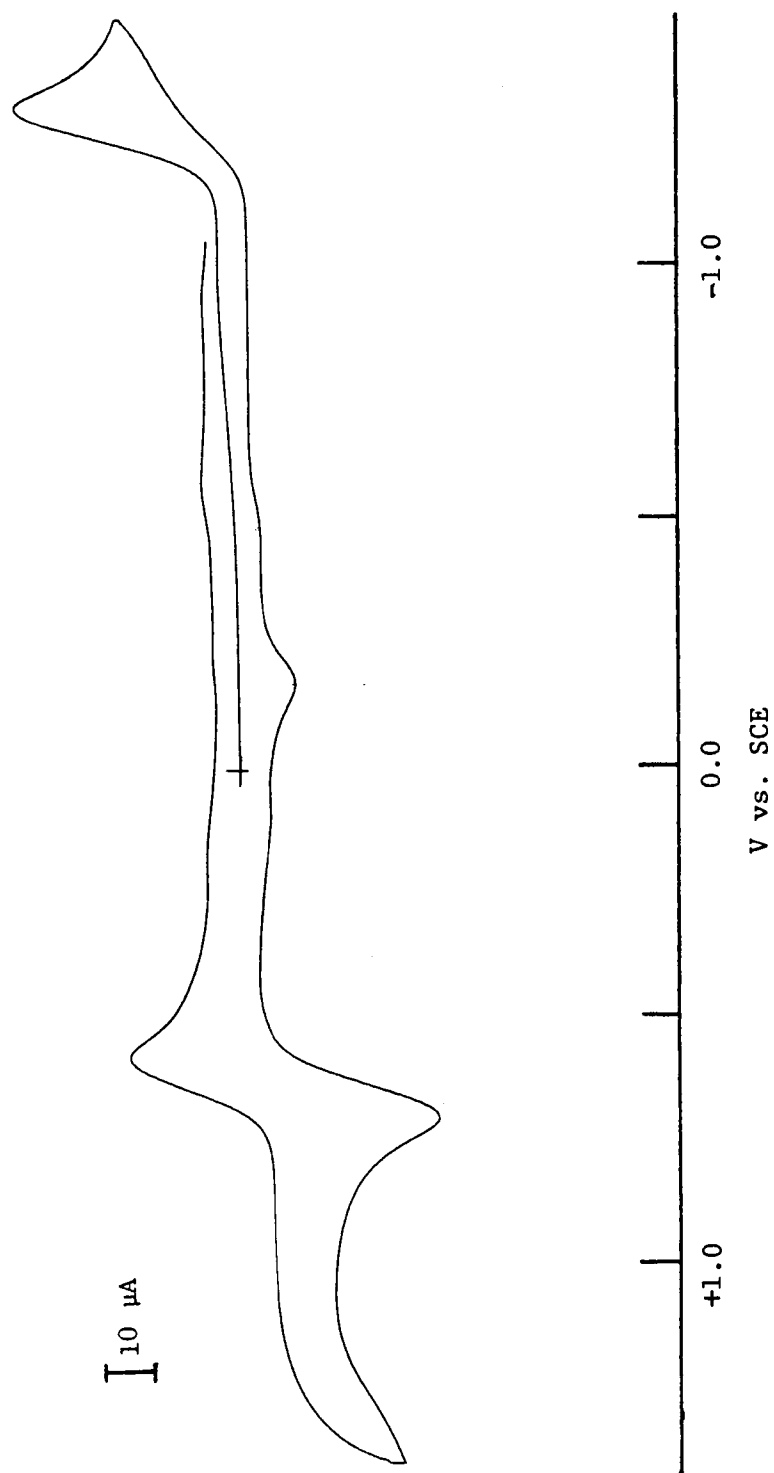


Figure 13. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$.

rhodium isocyanide complexes 3.^{81,82} The ill-defined oxidation peaks at -0.18 and -0.48 V are associated with the reduction peak at -1.3 V.

For the couple centered near +0.64 V in Figure 13, ΔE (the separation between the cathodic and anodic peaks) increases with sweep rate while the $E_{1/2}$ (the mean of E_{pa} and E_{pc}) remains unchanged (Table V). This behavior is consistent with a quasi-reversible electron transfer.⁸³ A quasi-reversible electron transfer is a process in which the rate constants for the oxidation and reduction reactions are of the same order of magnitude and in which the electron transfer is slow relative to the potential sweep rate.^{84,85} A plot of the anodic peak current (i_{pa}) vs. $v^{1/2}$ (the square root of the sweep rate) for the couple in Figure 12 deviates slightly from linearity (Figure 14) and the current ratios i_{pc}/i_{pa} are less than one (Table V) for sweep rates from 10 to 200 mV S⁻¹. This behavior is in agreement with that seen by Womack⁸¹ for tetrakis(isocyanide) binuclear rhodium complexes.

The quasi-reversible couple centered near +0.6 V has been shown by Womack⁸¹ to correspond to a one-electron transfer process ($n = 1$). Controlled potential electrolysis of deep blue 25 at approximately +0.9 V results in a dark yellow oxidation product. This product does not exhibit the reduction peak at 0.58 V (Figure 13) but does exhibit several ill-defined reduction peaks at more negative potentials.⁸¹ The disappearance of the cathodic component of the quasi-reversible couple is indicative of a follow-up reaction that is not seen on the voltammetric time scale. Although this follow-up process appears to

TABLE V
VOLTAMMETRIC DATA FOR $[(\underline{i}\text{-C}_3\text{H}_7\text{NC})_4\text{Rh}_2(\text{DPM})_2](\text{PF}_6)_2$

v , mV/S	E_{pa}	E_{pc}	ΔE	$E_{1/2}$	i_{pc} , μA	i_{pa} , μA	$i_{\text{pc}}/i_{\text{pa}}$
200	0.72	0.57	0.15	0.64	48	55	0.87
100	0.70	0.57	0.13	0.63	34	39	0.87
50	0.69	0.58	0.11	0.63	25	29	0.86
20	0.68	0.60	0.08	0.64	16.5	18.5	0.89
10	0.68	0.60	0.08	0.64	11	13	0.85

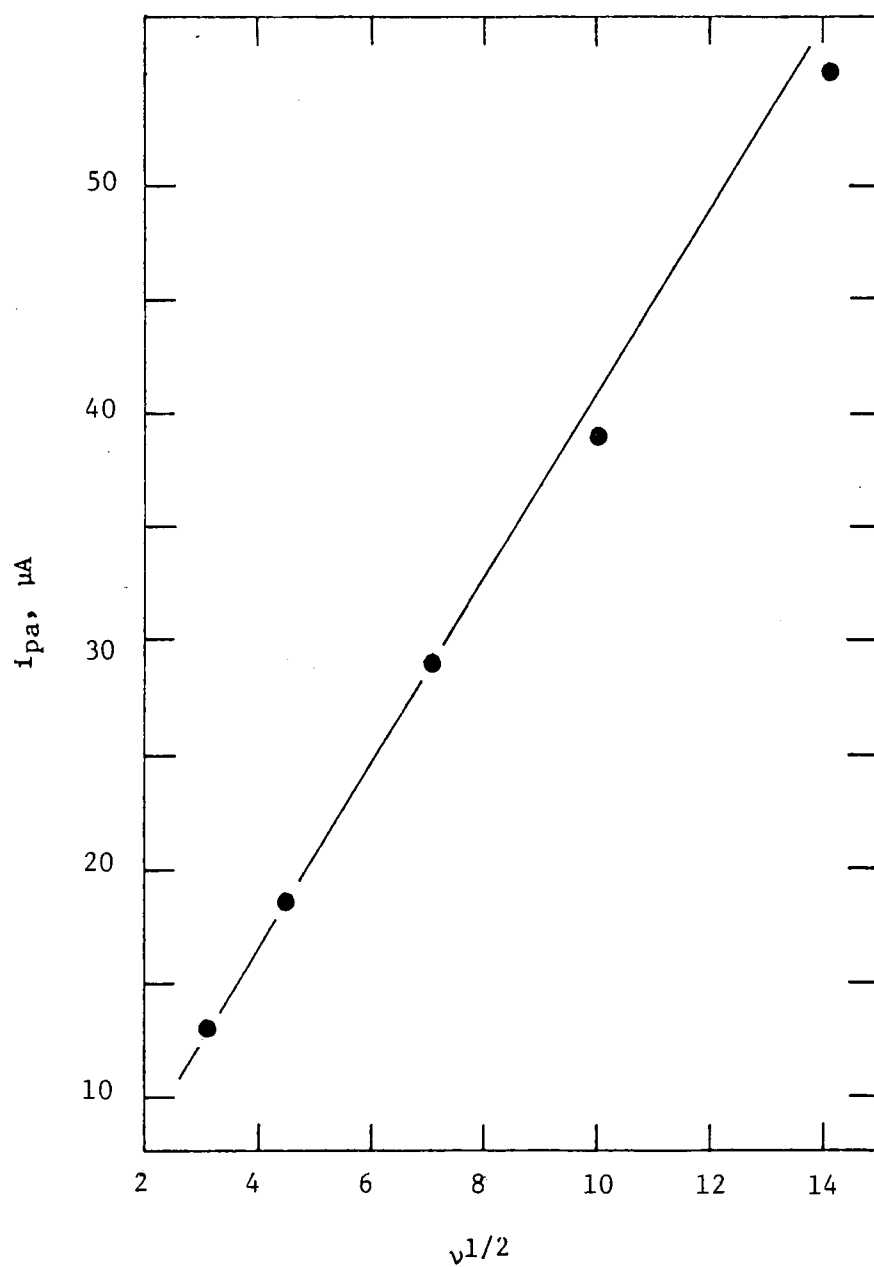


Figure 14. Plot of the anodic peak current (i_{pa}) vs. $v^{1/2}$ for the quasi-reversible couple in Figure 13 (page 85).

produce an uncharacterizable mixture of products, the original rhodium complex can be regenerated through electrochemical reduction of these products.^{81,82} Therefore, the integrity of the dimeric structure of the rhodium complex is apparently maintained throughout the electron transfer process.

Exhaustive electrolysis past the second oxidation peak of binuclear tetrakis(isocyanide) rhodium complexes is not possible in CH_2Cl_2 due to the close proximity of the oxidation peak to the solvent limit (Figure 13, page 85). However, it was thought that the presence of a coordinating species would stabilize the resulting Rh(II) complex, facilitating the removal of the second electron, thus shifting the second oxidation peak to less positive values.

The cyclic voltammogram of 25 in CH_2Cl_2 and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ with a 1:2 mole ratio of $(\text{C}_4\text{H}_9)_4\text{NCl}$ present is shown in Figure 15. The quasi-reversible couple that was observed in the absence of chloride ion has disappeared. A single oxidation peak at +0.52 V and two reduction peaks at -0.32 and -0.66V now appear. The couples centered at approximately +0.9 and +1.25 V are due to the chloride ion. Exhaustive controlled potential electrolysis at +0.75 V indicated that the oxidation peak at +0.52 V represents a two-electron transfer ($n = 2.00 \pm 0.03$). Figure 16 shows the voltammogram after oxidation at +0.75 V. The Rh(I) species responsible for the oxidation peak at +0.52 V is initially absent but is regenerated after reduction of the species giving rise to the reduction peaks at -0.32 and -0.66 V. Therefore, the dimeric framework of the rhodium complex is

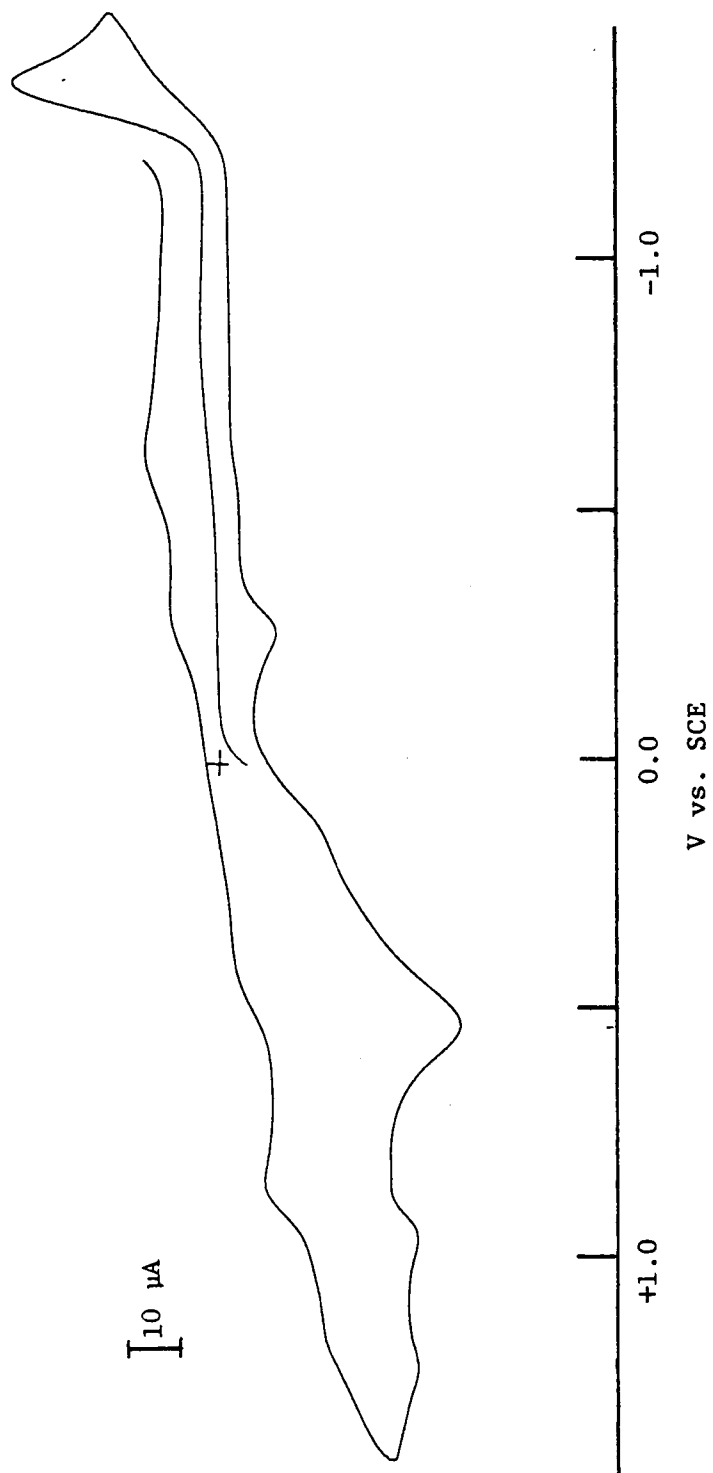


Figure 15. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\bar{i}\text{-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $\text{C}_4\text{H}_9)_4\text{PF}_6$, and 4×10^{-3} M $(\text{C}_4\text{H}_9)_4\text{NCl}$.

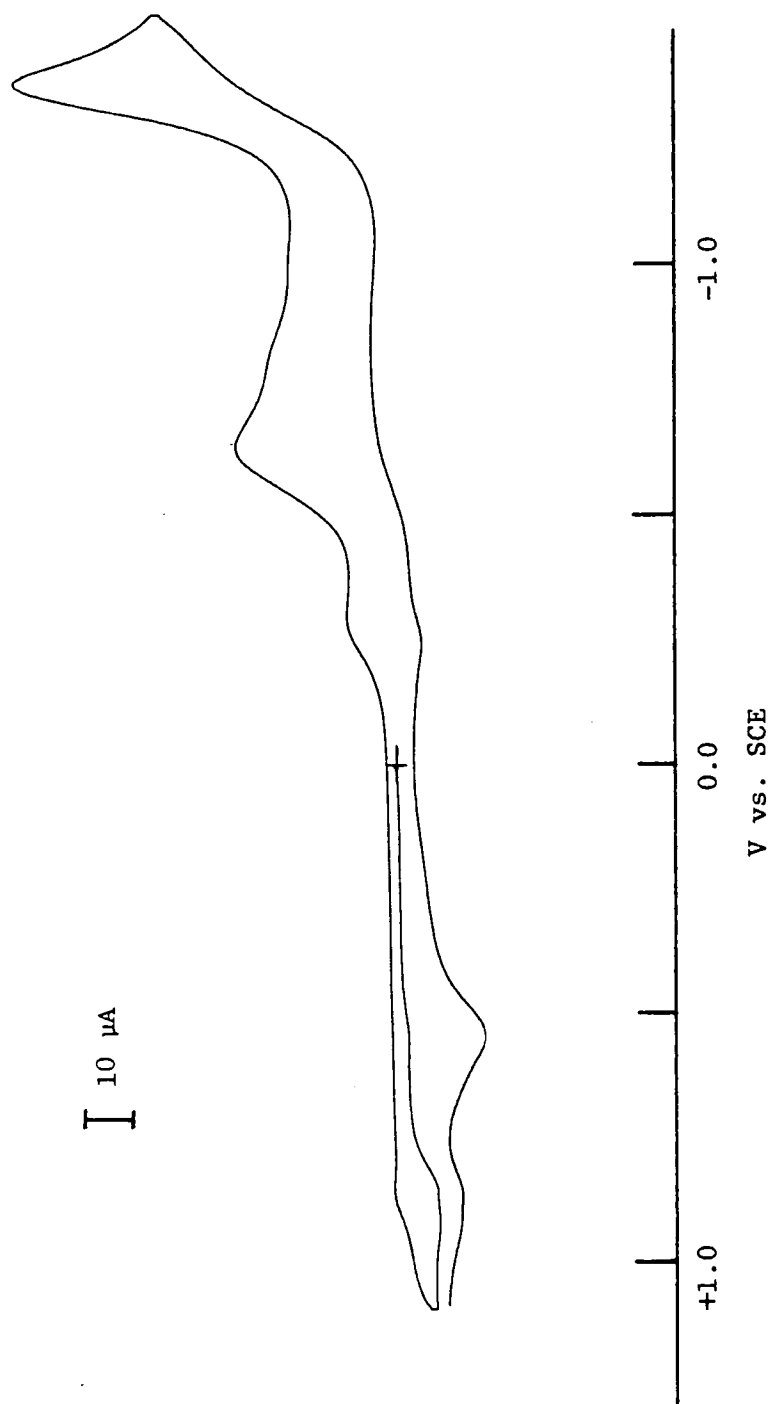


Figure 16. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M $(\text{C}_4\text{H}_9)_4\text{NCl}$ after oxidation at +0.75 V.

apparently retained after the two-electron transfer as it was in the case of the one-electron transfer process mentioned previously.

The oxidation product resulting from the electrolysis was originally thought to be compound 55, the Rh(II) analogue of 25, in which chloride ions have coordinated to the metal centers producing the octahedral environment preferred by Rh(II). Electrolyses of 25 in the presence of the chloride ion often showed only one reduction peak at -0.60 V rather than the two reduction waves in Figure 16. Figure 17 shows the voltammogram of a system containing 25 in excess $(C_4H_9)_4NCl$ after oxidation at $+0.75$ V. The concentration of 25 in the solution whose voltammogram is shown in Figure 17 is much greater than that in the solutions given the voltammogram shown in Figure 16 and therefore the oxidation took a longer period of time to complete (ca. 2 hours vs. 40 minutes). The system consisting of compound 25 and excess chloride ions was then investigated at low temperatures to determine whether the reduction peak near -0.60 V represented a species resulting from a follow-up reaction.

Figure 18 shows the voltammograms of 25 at $20.4^\circ \pm 0.2^\circ C$ in CH_2Cl_2 with a two-fold molar ratio of butylpyridinium chloride present. The two-electron oxidation (ox) peak occurs at approximately $+0.5$ V to give the species responsible for the reduction waves at -0.35 and -0.72 V (R_1 and R_2 , respectively). As the temperature of the system represented by Figure 18 is lowered, the ratio of the peak currents for R_1 and R_2 changes dramatically until R_2 essentially disappears at approximately -40° as demonstrated by Figure 19.

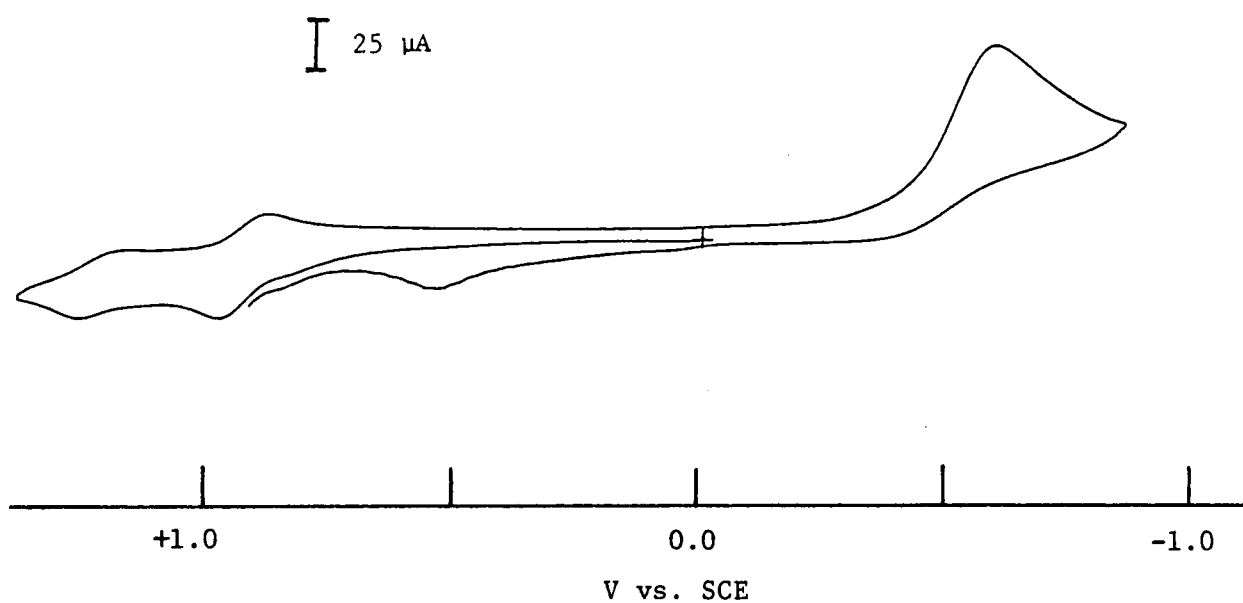


Figure 17. Cyclic voltammogram of $2.5 \times 10^{-3} \text{ M}$ $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{N}(\text{PF}_6)_2$, and 10^{-2} M $(\text{C}_4\text{H}_9)_4\text{NCl}$ after oxidation at $+0.75 \text{ V}$.

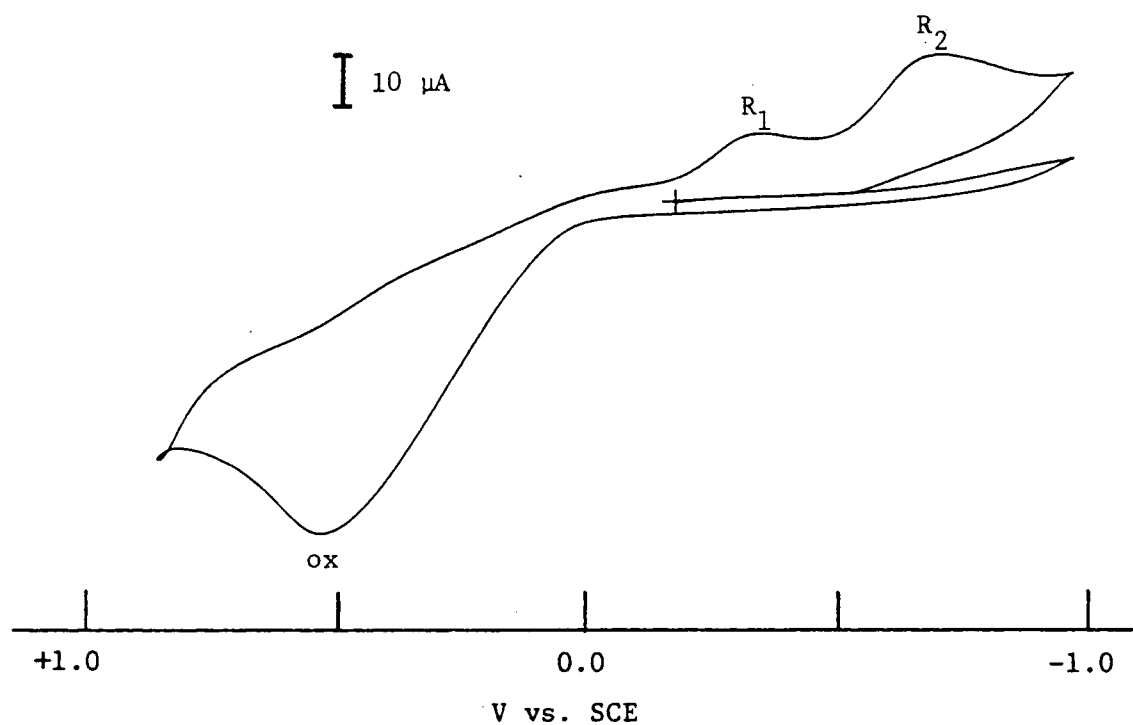


Figure 18. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M $[(\text{C}_5\text{H}_4\text{N})\text{C}_4\text{H}_9]\text{Cl}$ (temperature = $20.4 \pm 0.2^\circ\text{C}$).

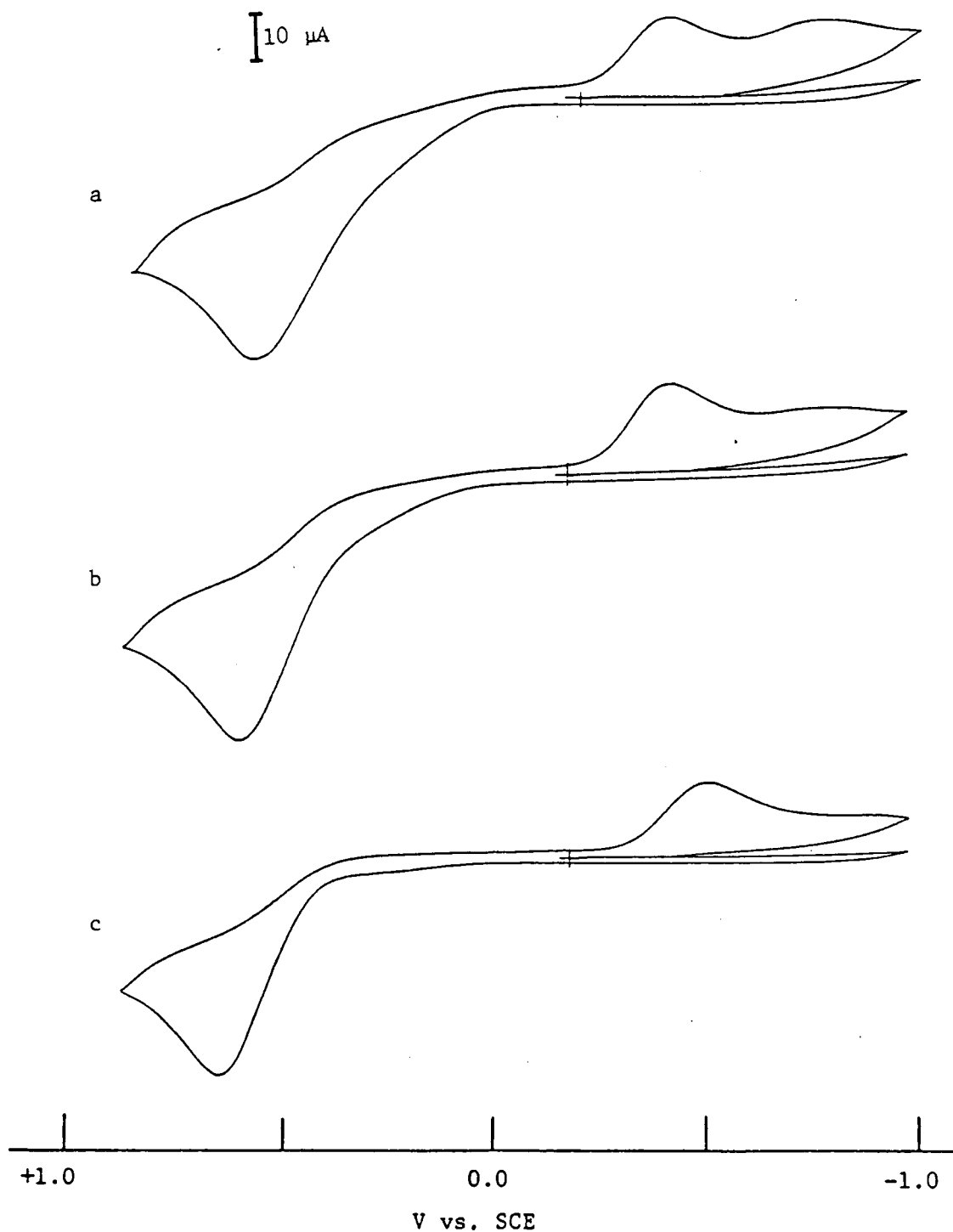


Figure 19. Cyclic voltammograms of $10^{-3} \text{ M } [\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4 (\text{DPM})_2]-(\text{PF}_6)_2$ in CH_2Cl_2 , $0.1 \text{ M } (\text{C}_4\text{H}_9)_4 \text{ N PF}_6$, and $4 \times 10^{-3} \text{ M } [(\text{C}_5\text{H}_4\text{N})\text{C}_4\text{H}_9]\text{Cl}$ at various temperatures: (a) $6.4 \pm 0.2^\circ\text{C}$; (b) $-10.7 \pm 0.02^\circ\text{C}$; and (c) $-39.7 \pm 0.2^\circ\text{C}$.

Therefore, it appears that the reduction wave R_2 is due to a species resulting from a follow-up reaction involving the species that gives rise to R_1 in Figure 18. The species initially produced by the oxidation of 25 in the presence of the chloride ion may indeed be the dichloride complex 55, which then undergoes a further reaction with other species in the solution. Elemental analyses of the products obtained from the electrolysis of either the hexafluorophosphate or tetrafluoroborate salt of 25 were not consistent with the formulation of the product as 55. It appears that the follow-up reactions leads to the formation of an uncharacterizable mixture of products.

In the electrochemical synthesis of binuclear tetrakisocyanide Rh(II) complexes, the separation of the desired product from the supporting electrolyte proved extremely difficult. Attempts to isolate the oxidation product from the supporting electrolyte on the basis of solubility differences were not possible using a wide variety of solvents; therefore, chromatographic separation methods were attempted. When the product resulting from a two-electron oxidation of 25 in the presence of tetrabutylammonium chloride and 0.1 M $(C_4H_9)_4NPF_6$ was placed on a column consisting of neutral alumina, the red-brown mixture immediately changed to the deep blue color of the original complex. The rhodium dimer remained stationary on the column as a blue band while the $(C_4H_9)_4NPF_6$ was eluted with CH_2Cl_2 . The blue-purple compound eluted rapidly with 10% water in acetone. The complex eluted from the column gave a UV-visible spectrum identical to the original rhodium(I) complex: hence, the oxidation product was

reduced, probably by the alumina, back to compound 25. The reduction of the electrolysis product probably involves the concomitant abstraction of halide ions from the dimer by the alumina. Such a process should be possible since acidic and basic sites are present in neutral alumina,⁸⁶ and it has been shown that surface hydroxyl groups are capable of undergoing electron transfer with absorbed molecules.⁸⁷ It has also been shown that basic hydroxyl groups can exchange with other anions.⁸⁶

In view of the difficulties involved in the isolation of the PF_6^- salts of the electrochemical oxidation products of the Rh(I) complexes, the BF_4^- salts of these compounds were used. The electrochemistry of the BF_4^- salts of the rhodium dimers is essentially the same as that of the PF_6^- complexes,⁸¹ but the tetrafluoroborate electrolyte, $(\text{C}_4\text{H}_9)_4\text{NBF}_4$, is sparingly soluble in warm water and therefore should allow for easier separation of the oxidation products from the supporting electrolyte. Although attempts to oxidize 26, the BF_4^- analogue of 25, in the presence of $(\text{C}_4\text{H}_9)_4\text{NCl}$ resulted in readily isolable oxidation products, elemental analyses of these products were not consistent with their formulation as the rhodium(II) dichloro complex of type 24. The oxidation of 26 appears to result in a mixture of products analogous to the products of 25 obtained from the oxidation in the presence of chloride ions.

This investigation has not led to a characterizable Rh(II) dichloride complex of type 24 by either chemical, photochemical, or electrochemical oxidation of the Rh(I) precursor. The lack of any

reported data on compounds like 24 may indicate that the synthesis of such complexes is not possible in spite of their similarity to the dichloro Rh(II) binuclear complex 20 reported by Gray and coworkers.^{15,53,54}

C. Electrochemical Behavior of Tetrakisisonocyanide Complexes in Acetonitrile

Figure 20 shows the cyclic voltammogram of 25 in CH₃CN and 0.1 M (C₄H₉)₄NPF₆ and illustrates an electrochemical behavior that is typical of the tetrakisisonocyanide rhodium complexes of type 3.^{81,82} Since acetonitrile can coordinate to metal centers much more readily than dichloromethane, the electrochemical behavior of 25 differs greatly in the two solvents as seen in a comparison of Figures 13 (page 85) and 20. Displayed in Figure 20 are two oxidation peaks at about +0.6 and +1.0 V and two poorly resolved reduction peaks that are coupled to the oxidation peak at +1.0 V. If the potential scan is reversed immediately after the oxidation wave at +0.60 V, a reduction peak at +0.24 V appears⁸¹ that is apparently due to a quasi-reversible electron transfer process, while the ill-defined reduction peaks that appear upon sweeping through the second oxidation peak are absent. Womack⁸¹ has demonstrated that the second oxidation peak in Figure 20 is due to the removal of a second electron from the rhodium complex, since controlled potential electrolysis at +1.3 V for this system indicates a two-electron transfer concomitant with a color change of deep blue to pale yellow. This color change is

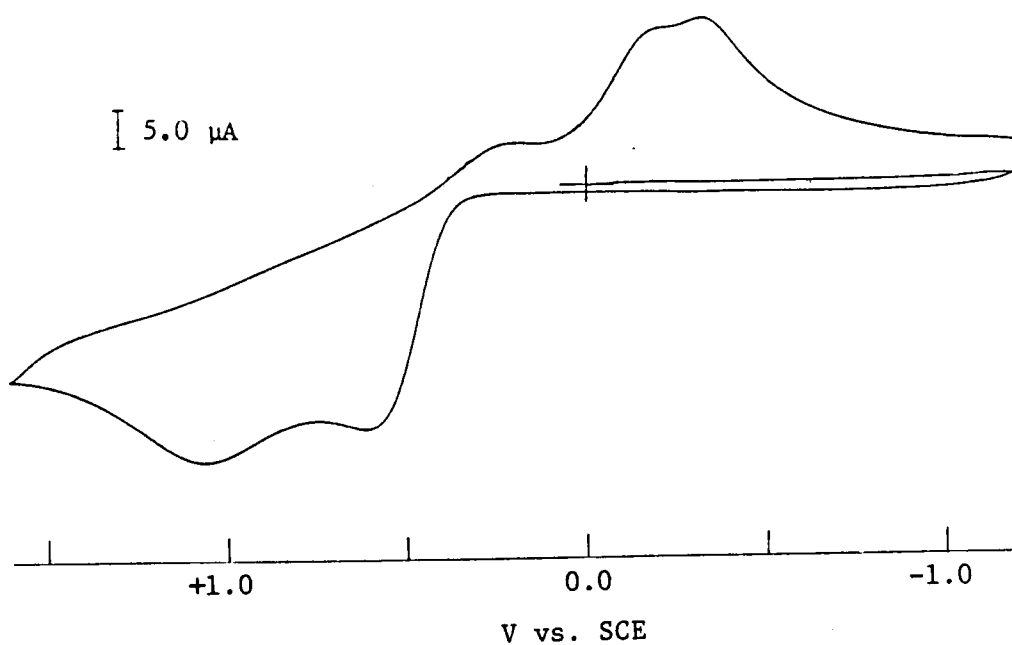
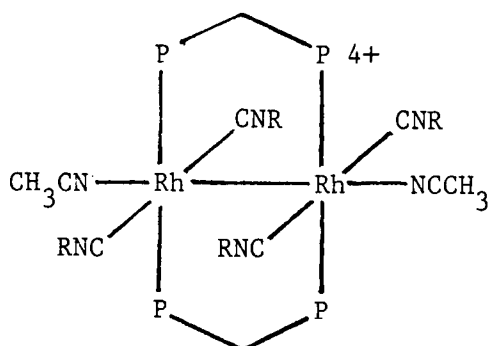


Figure 20. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_3CN and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$.

characteristic of oxidation of the dimer from a Rh(I) to a Rh(II) complex.² Figure 21 shows the voltammogram of 25 after controlled potential electrolysis at +1.3 V. Sweeping through the resulting reduction waves appearing at -0.20 and -0.32 V produces two oxidation peaks that are similar to the peaks in the original complex plus a third oxidation peak at about +1.4 V. Therefore, the reduction of the species resulting from the oxidation of 25 is either slow on the voltammetric time scale or may be accompanied by a follow-up reaction.

The oxidation of the complex $[\text{Rh}_2(\underline{n}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{BF}_4)_2$, 57, at +1.0 V via controlled potential electrolysis results in a yellow Rh(II) complex which is most likely stabilized by coordination to CH_3CN and is therefore formulated as 58. Some evidence for the existence of complexes such as 58 has been presented by Womack,⁸¹ who has formulated the two-electron oxidation product of 26 isolated from



58; R = n-C₄H₉

CH_3CN as $[\text{Rh}_2(\underline{i}\text{-C}_3\text{H}_7\text{CN})_4(\text{DPM})_2][\text{BF}_4]_4 \cdot 0.5\text{CH}_3\text{CN}$. Addition of $\text{C}_4\text{H}_9\text{NI}$ to the oxidized CH_3CN solution of 57 results in a red solution that gives a UV-visible spectrum that is identical to the one reported by Balch²

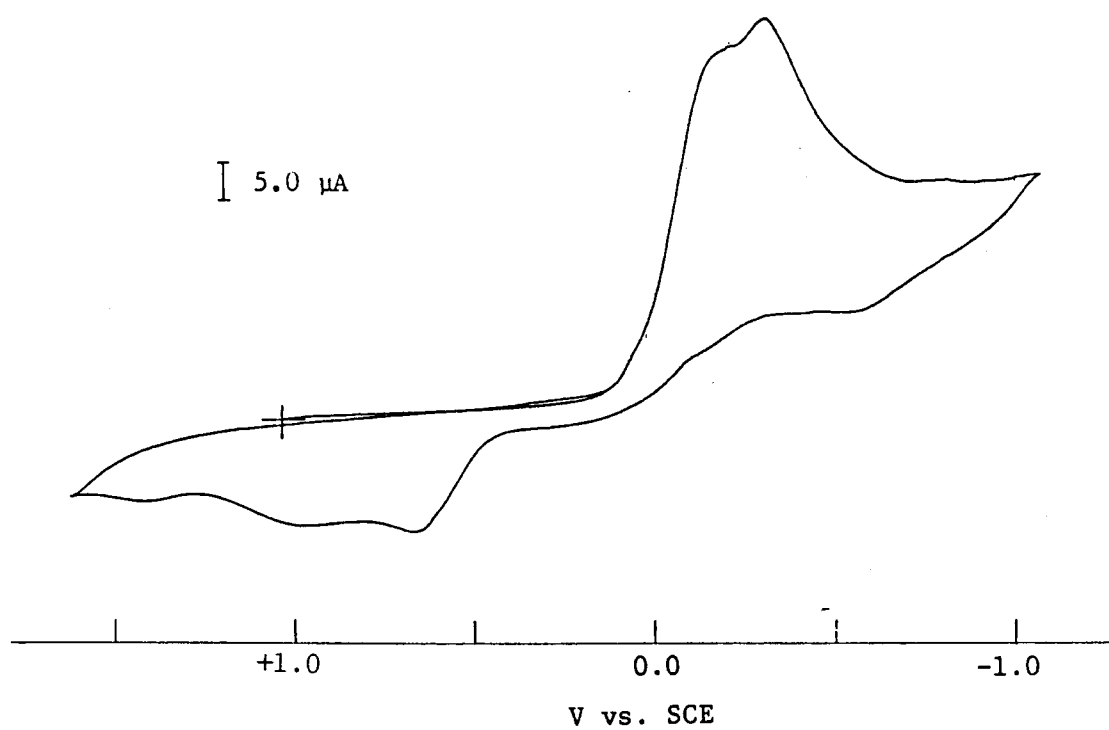


Figure 21. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_3CN and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ after oxidation at +1.3 V.

for $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2\text{I}_2][\text{PF}_6]_2$. Therefore, the complex resulting from the addition of I^- to 58 is formulated as 56.

The synthesis of stable Rh(II) complexes such as 56 by the addition of a halogen to 58 suggested the possibility of producing new complexes through the addition of other coordinating anions to 58. The addition of $\text{C}_4\text{H}_9\text{NSCN}$ and $\text{C}_4\text{H}_9\text{NCN}$ to the isopropyl analogue of 58 in CH_3CN produced complexes that analyze as $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2(\text{SCN})_2][\text{BF}_4]_2$, 59, and $[\text{Rh}_2(\text{i-C}_3\text{H}_7\text{NC})_4(\text{DPM})_2](\text{CN})_2[\text{BF}_4]_2$, 60, respectively. These compounds exhibit isocyanide stretching frequencies at 2194 cm^{-1} and 2182 cm^{-1} for 59 and 2203 cm^{-1} for 60 (compared with 2169 cm^{-1} and 2147 cm^{-1} for the Rh(I) complex). These shifts in isocyanide stretching frequencies are consistent with the oxidation of Rh(I) species to Rh(II) species. Complex 59 displays IR bands at 2094 cm^{-1} and 2050 cm^{-1} which have been assigned to the $\nu(\text{CN})$ of the SCN^- ligands. Since these frequencies appear in a region that is common to the ranges in which $\nu(\text{CN})$ frequencies occur for both S-bonded and N-bonded SCN^- complexes,^{88,89} the bonding mode of the thiocyanate ligands cannot be conclusively determined from IR data. However, the absence of any strong bands from a C-S stretch in the 800 cm^{-1} region may indicate that the SCN^- ligands are S-bonded.⁸⁹ Complex 60 did not exhibit any IR bands that could be assigned conclusively to the CN ligands. Although the geometries of compounds 59 and 60 are not definitely known, it is reasonable to assume that their structures are of the same type as compound 56 since the precursor for each of these complexes is 58.

D. Electrochemical Investigation of the Coordination of
Substituted Pyridines to Binuclear Rhodium(II)
Tetrakisocyanide Complexes

In view of the ability of binuclear rhodium tetrakisocyanide complexes to coordinate to anionic species such as I^- , CN^- , SCN^- , or neutral species such as CH_3CN upon oxidation of the rhodium centers, it is desirable to investigate the coordinating ability of other neutral ligands with the oxidation products of rhodium(I) dimers. Since over the years much interest has been shown in the coordination of substituted pyridines to transition metals,⁹⁰⁻⁹² the work presented in this chapter involves the electrochemical behavior of tetrakisocyanide rhodium(I) dimers in the presence of substituted pyridines. The degree of coordination of a pyridine to a metal center is dependent upon the Lewis basicity (or the orbital energy) of the lone pair on the ring nitrogen. Therefore, substituents on the pyridine ring that release electron density into the ring will increase the degree of association between the ring nitrogen and the metal,⁹³ while substituents that withdraw electron density from the ring will decrease the availability of the lone pair for bonding. These inductive effects are responsible for the general trend in the base strengths of the substituted pyridines shown in Table VI. Differences in the basicity of 3- and 4-substituted pyridines have been explained in terms of delocalization effects that are possible in 4-substituted pyridines but not in 3-substituted pyridines.⁹⁴

TABLE VI
AQUEOUS BASE STRENGTHS FOR SELECTED SUBSTITUTED PYRIDINES

Compound	pK_b^a
4-(dimethylamino)pyridine	4.29
3,4-dimethylpyridine	7.39
4-ethylpyridine	7.98
Pyridine	8.77
4-benzoylpyridine	10.65
4-cyanopyridine	12.12
3-cyanopyridine	12.55

^aThe base strength data for 3,4-dimethylpyridine and 4-ethylpyridine are taken from Reference 94. All other base strength data are taken from Reference 99.

However, the importance of delocalization effects upon the basicity of pyridines has recently been questioned.⁹⁵ Since the gas phase basicities of pyridine and 4-(dimethylamino)pyridine are greater than NH_3 , whereas their solution basicities are lower than that of NH_3 , it appears that several factors including solvent effects may be important in considering the strengths of solvated bases.⁹⁵⁻⁹⁷

Several investigators^{95,97,98} have demonstrated that plots of proton affinity (i.e., gas phase basicity) vs. enthalpy of protonation (i.e., aqueous basicity) for 3- and 4-substituted pyridines are linear. This implies that the proton affinities of 3- and 4-substituted pyridines all differ from their enthalpies of protonation by a constant amount, thus making the two values proportional to one another. Since the base strengths of the substituted pyridines in aqueous solutions are proportional to their gas phase basicities, the relative base strengths of a series of substituted pyridines in a non-aqueous solvent should be the same as in water. Therefore, the readily accessible base strength data for pyridines in aqueous solution should be applicable in CH_2Cl_2 .

The cyclic voltammogram of a 10^{-3} M solution of $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$, 27, in CH_2Cl_2 and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ is shown in Figure 22. The second oxidation peak occurs at about +1.3 V for 27 and is therefore much easier to measure than the corresponding peak for 25 which lies close to the solvent limit (see Figure 13, page 85). In the presence of a pyridine ligand, the potential of the second oxidation peak of 27 shifts dramatically to

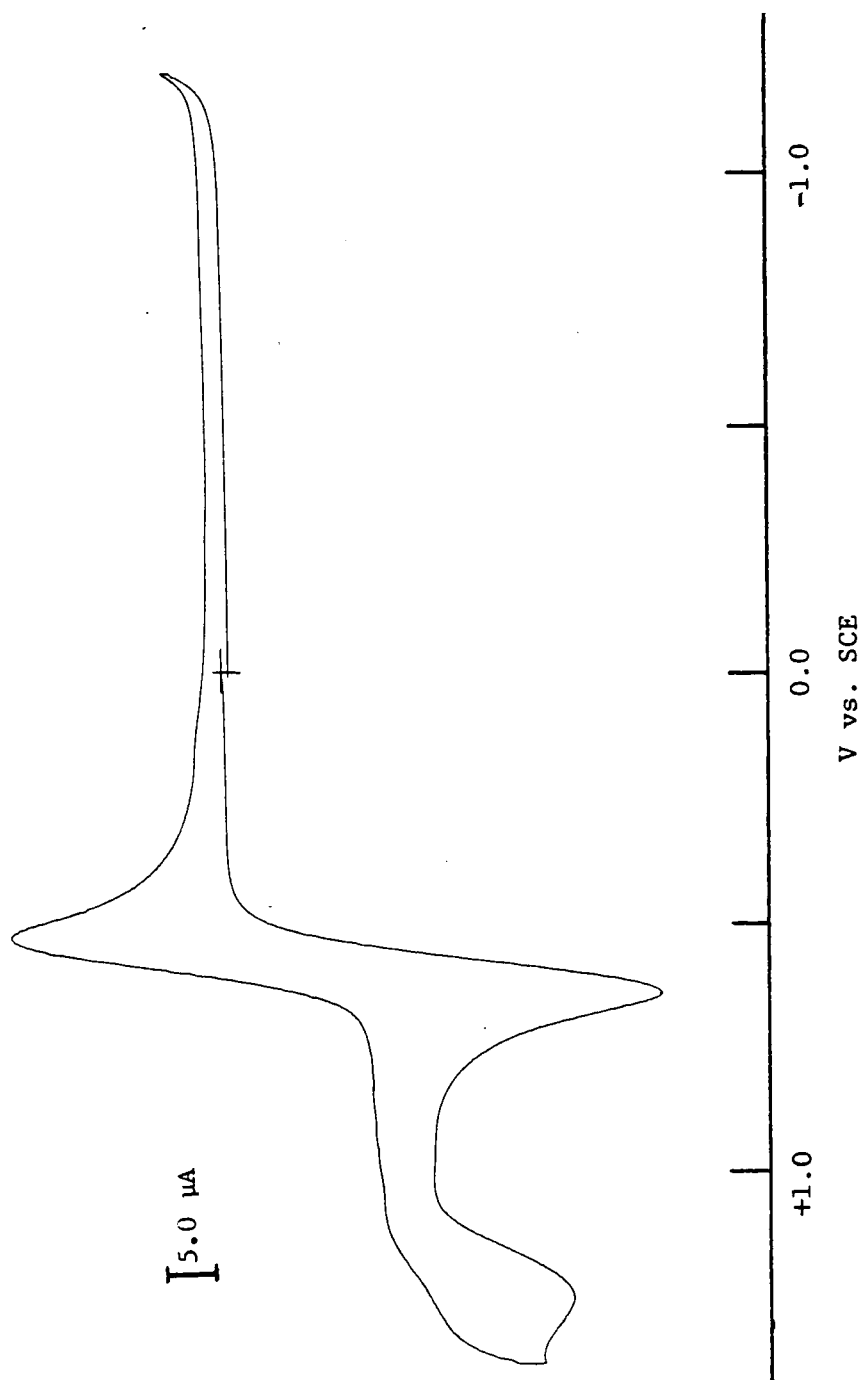
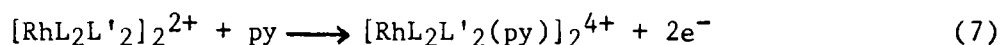


Figure 22. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$.

less positive values. This shift is indicative of coordination of the pyridine moiety to the rhodium complex.

The voltammograms of 27 in CH_2Cl_2 with varying amounts of the weak base 3-cyanopyridine present are shown in Figure 23. Figure 23a is the voltammogram with a 1:1 mole ratio of the pyridine to the rhodium complex. The oxidation peak at +1.3 V in Figure 13 (page 85) has shifted to an ill-defined peak at about +1.0 V while the couple centered at about +0.6 V remains essentially unchanged. If the amount of 3-cyanopyridine is increased to a 2:1 mole ratio, the second oxidation peak shifts slightly to a less positive potential and becomes much more well-defined as illustrated in Figure 23b. An increase in the amount of the pyridine present to a 4:1 mole ratio causes only a slight shift of the second oxidation potential, but produces a slightly more pronounced oxidation peak as shown in Figure 23c. Further addition of the pyridine beyond a 4:1 mole ratio does not produce any significant changes in either the potential or the shape of the oxidation peak. Therefore, this work examines the electrochemical behavior of 27 in the presence of 4:1 mole ratios (or 2-fold excesses) of the substituted pyridines. An excess of the pyridine tends to drive the coordination reaction between the pyridine and the rhodium complex in the direction of the coordinated complex (Equation 7). Also, an excess of the pyridine minimizes errors in



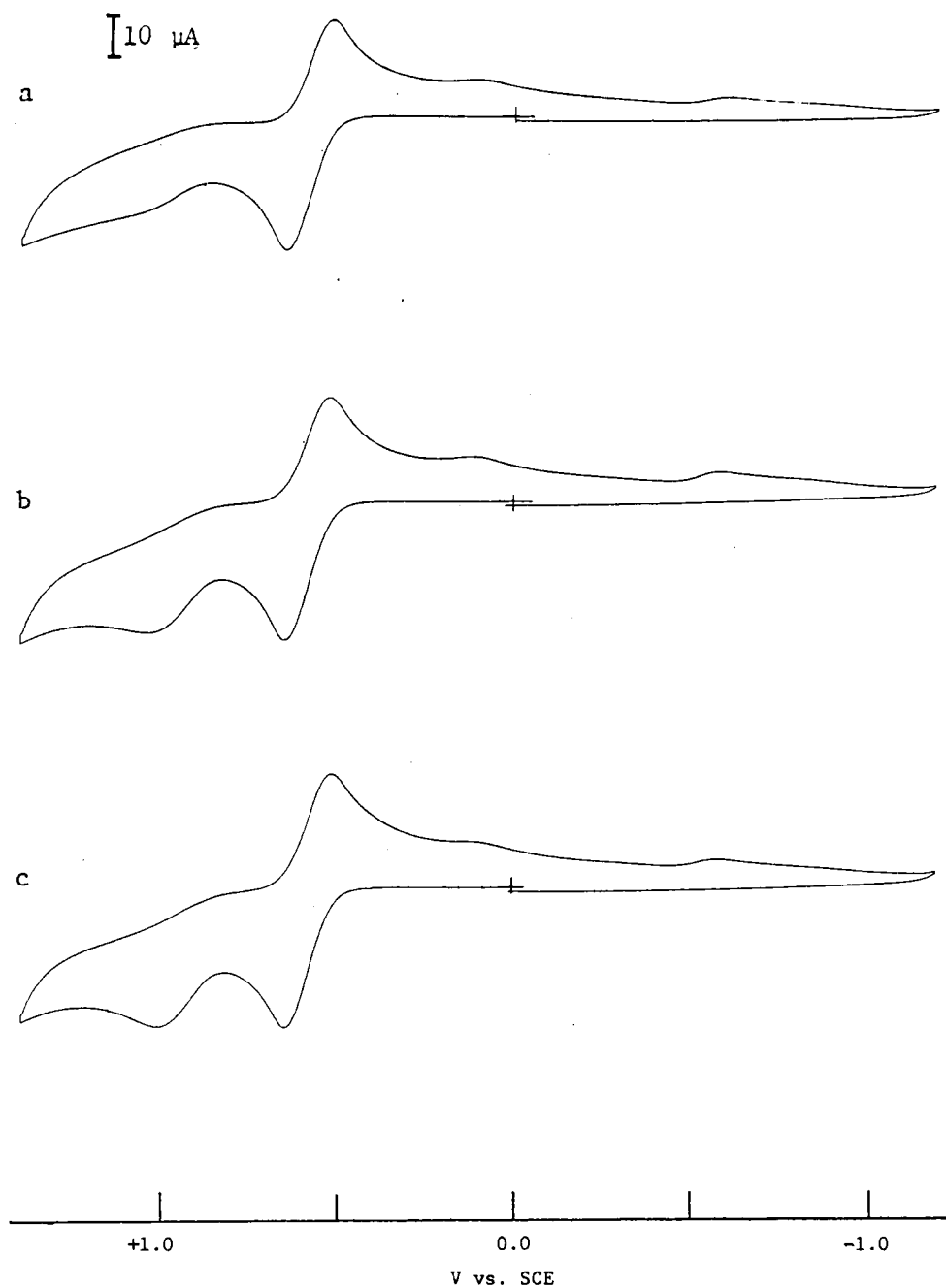


Figure 23. Cyclic voltammograms of 10^{-3} M $[\text{Rh}(\eta\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 ; 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$; and (a) 1×10^{-3} M 3-cyanopyridine; (b) 2×10^{-3} M 3-cyanopyridine; and (c) 4×10^{-3} M 3-cyanopyridine.

the measurement of the peak potentials since the peaks are better defined than in the cases where the pyridine are present in a 1:1 stoichiometry with the rhodium complex.

Figures 23c through 29 are the cyclic voltammograms of 27 with the substituted pyridines listed in Table VI (page 104) present in 4:1 molar ratios. There are two general trends evident in these voltammograms, each being a function of the base strength of the substituted pyridines. The first is the disappearance of the reduction component of the quasi-reversible couple centered at about +0.6 V after scanning through the second oxidation peak. The decrease in peak current of the reduction component is more pronounced for the stronger bases. The second general trend is a shift in the potential of the second oxidation peak to less positive values as the basicity of the pyridine increases, while the first oxidation peak shifts only slightly compared to the shift in the second oxidation peak.

The quasi-reversible nature of the couple centered near +0.6 V is evident in Figures 23C and 24 for the systems containing 3- and 4-cyanopyridine, respectively. However, as noted earlier, the base strength of the substituted pyridine increases (see Figures 24 and 29), the quasi-reversible nature of the couple decreases upon sweeping through the second oxidation peak, until the reduction component of the couple no longer appears for the relatively strong base 4-dimethylaminopyridine (Figure 29). Investigations with pyridine demonstrate that the quasi-reversible nature of the couple is partially retained if the second oxidation peak is not scanned

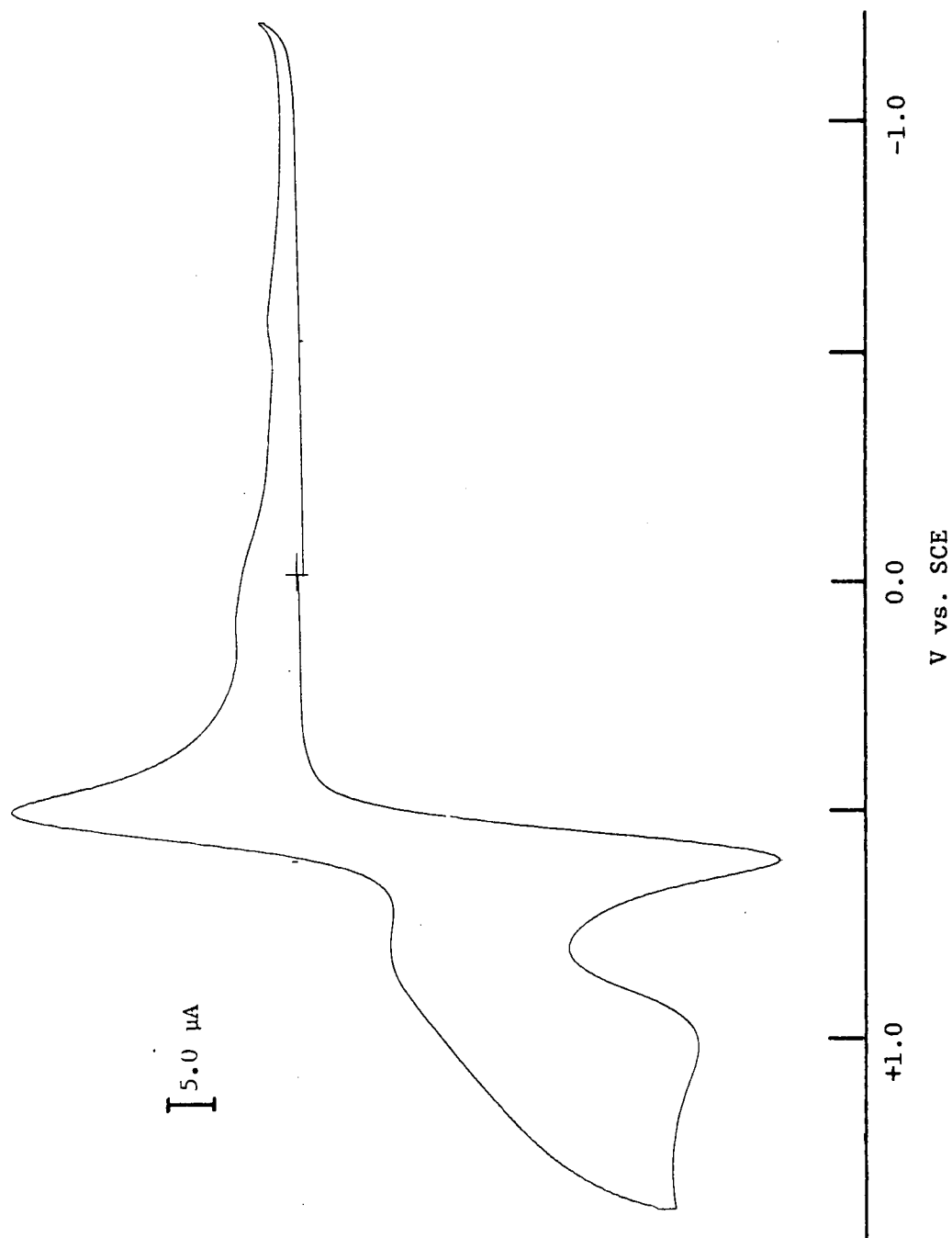


Figure 24. Cyclic voltammogram of 10^{-3} M $[Rh_2(\bar{n}\text{-C}_4\text{H}_9\text{NC})_4Rh_2(\text{DPM})_2](PF_6)_2$ in CH_2Cl_2 , 0.1 M $(C_4H_9)_4NPF_6$, and 4×10^{-3} M 4-cyanopyridine.

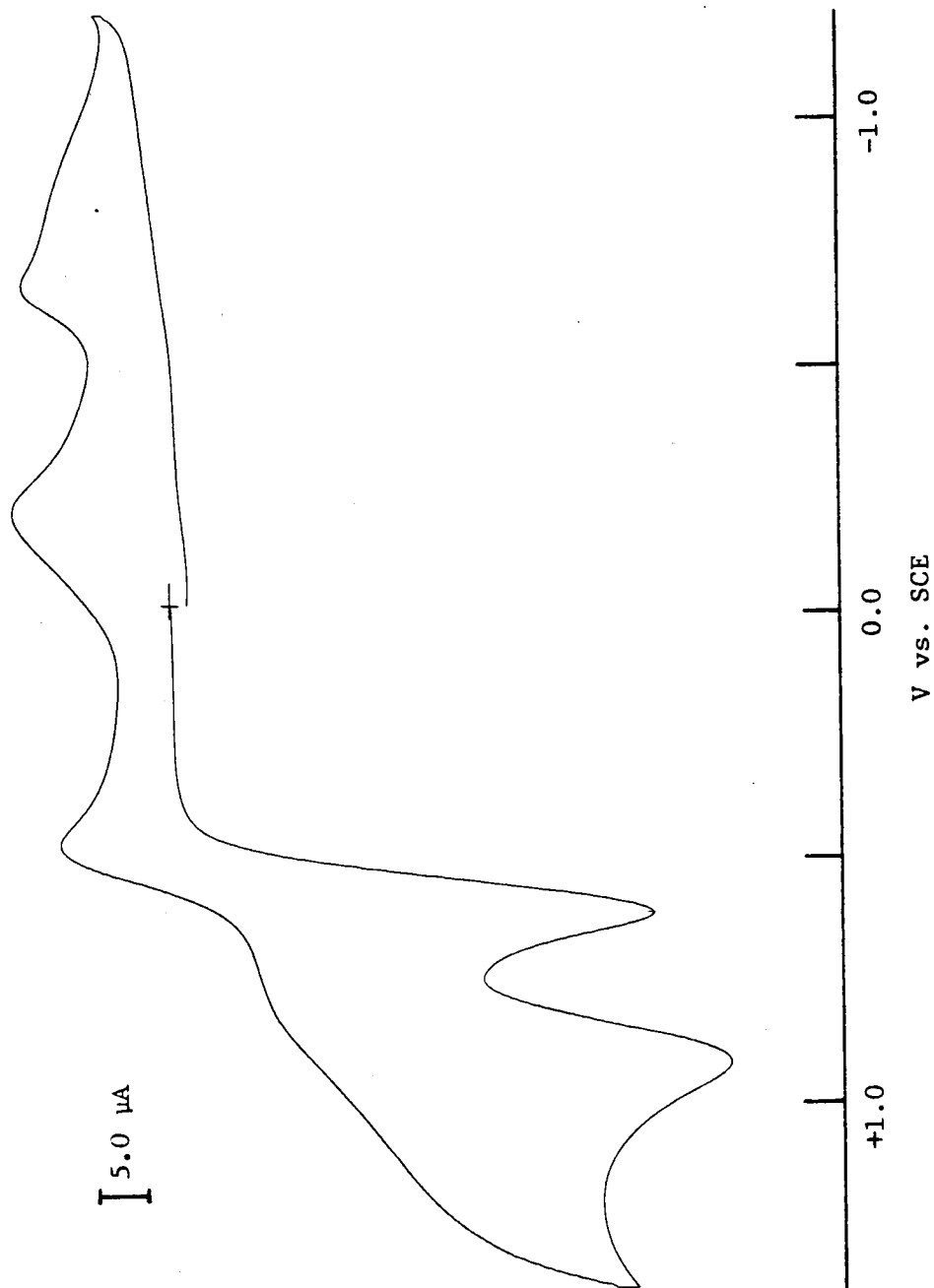


Figure 25. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M 4-benzoylpyridine.

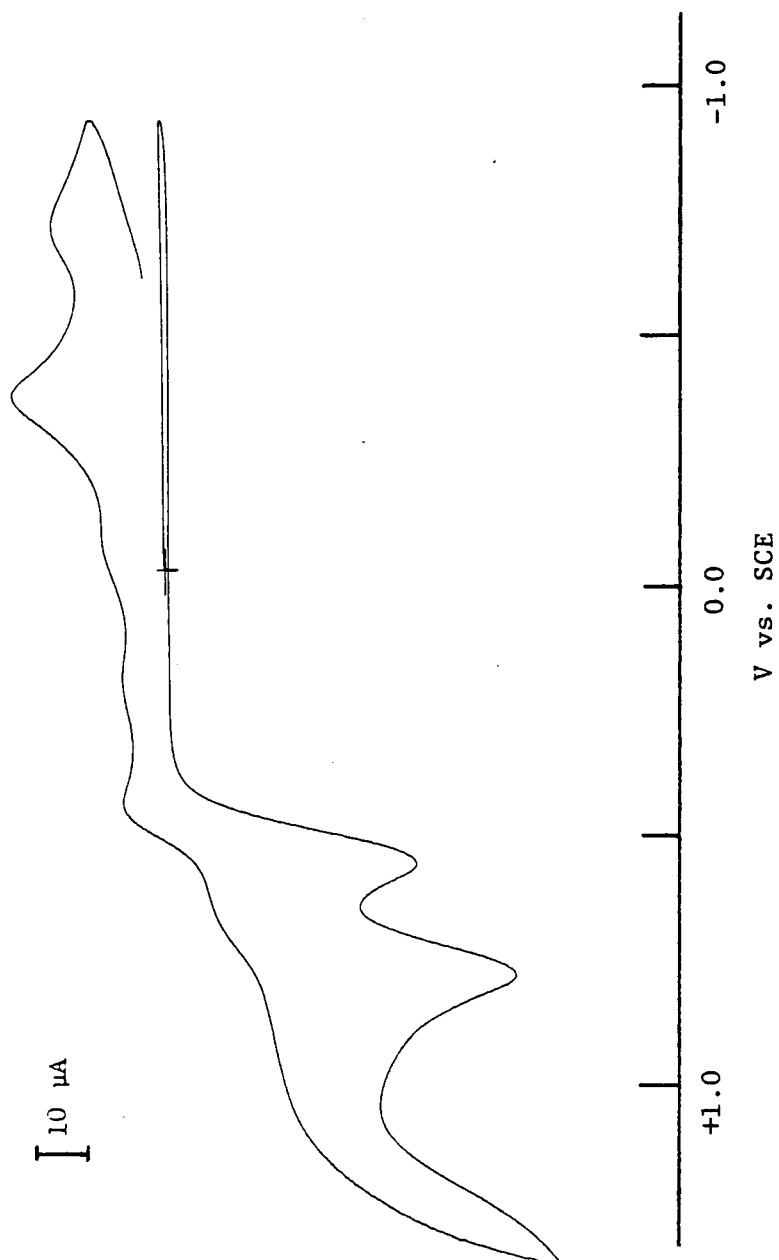


Figure 26. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ and 4×10^{-3} M pyridine.

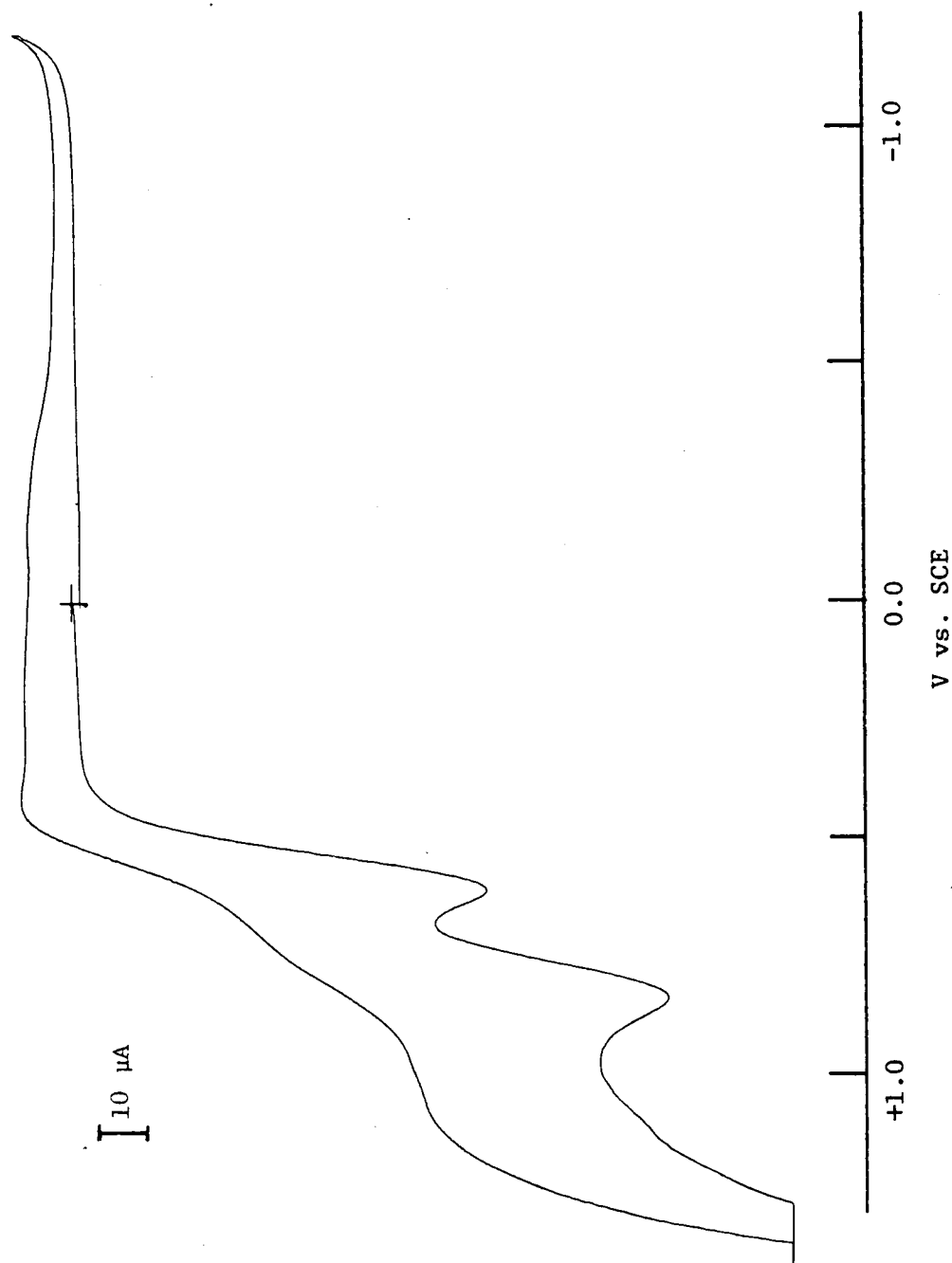


Figure 27. Cyclic voltammogram of 10^{-3} M $[Rh_2(n-C_4H_9NC)_4(DPM)_2](PF_6)_2$ in CH_2Cl_2 , 0.1 M $(C_4H_9)_4NPF_6$, and 4×10^{-3} M 4-ethylpyridine.

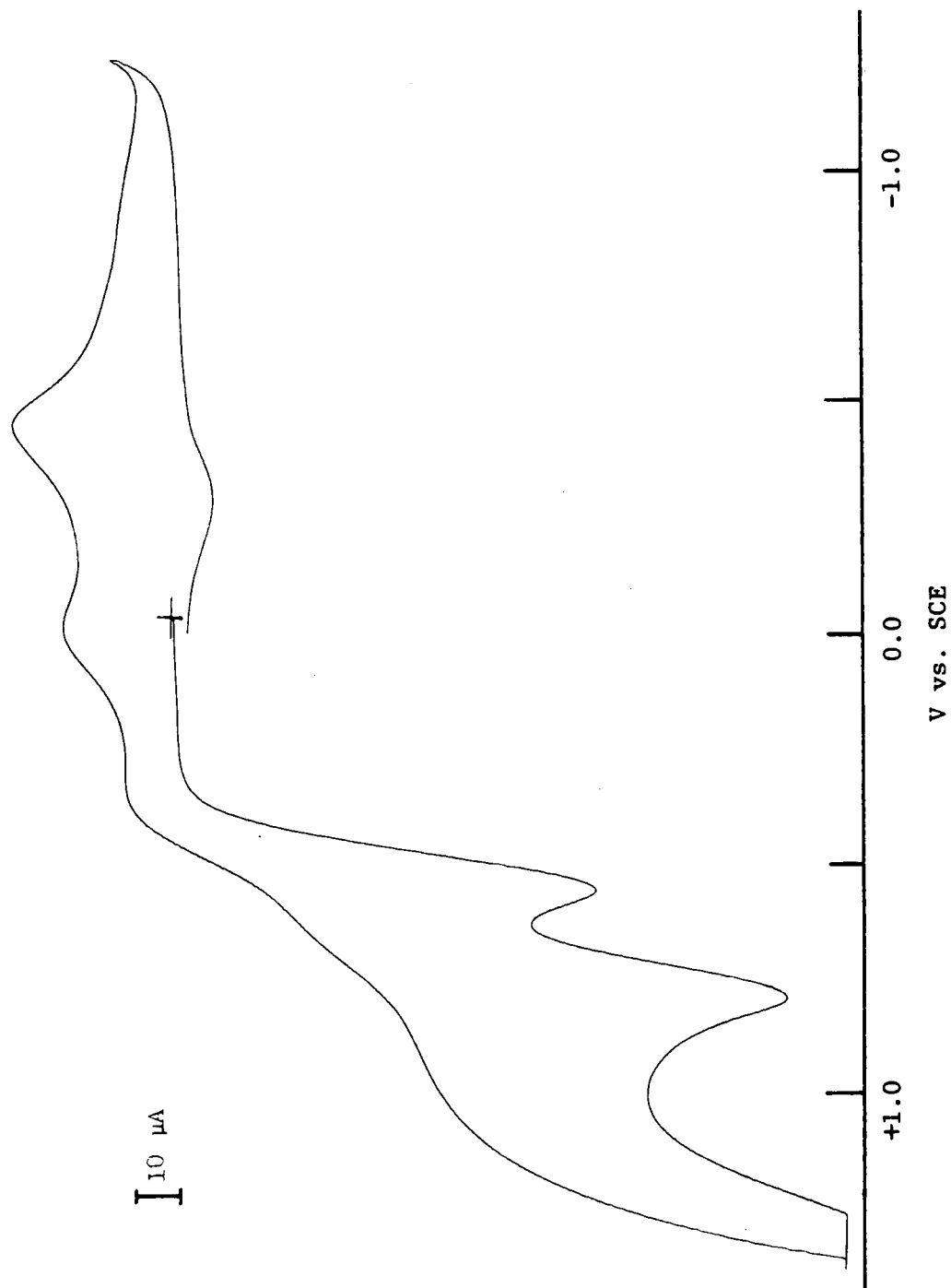


Figure 28. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\bar{\text{n}}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M 3,4-dimethylpyridine.

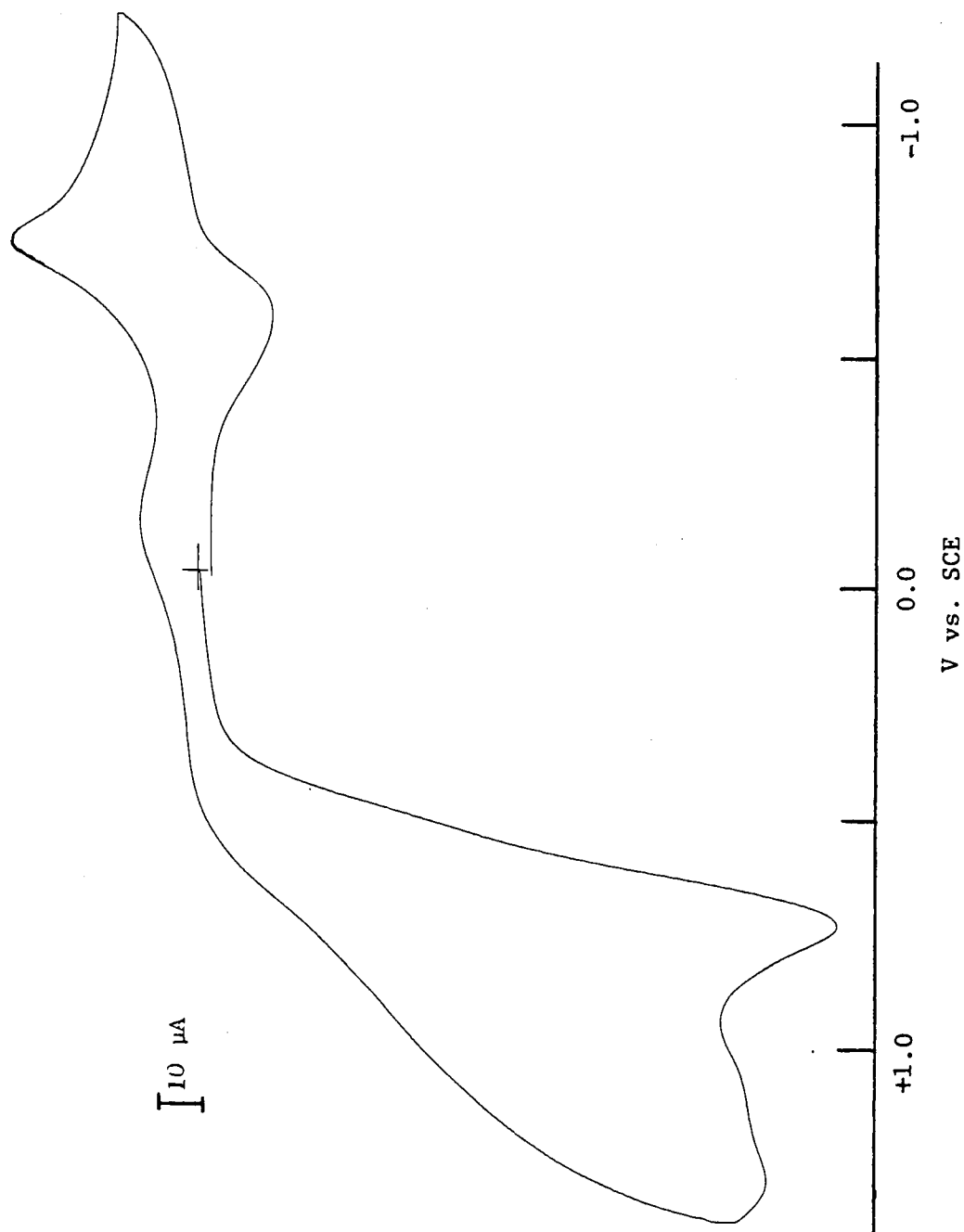
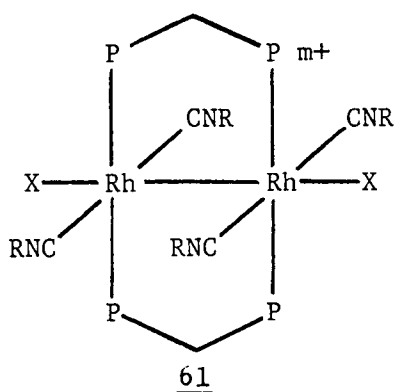


Figure 29. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M 4-(dimethylamino) pyridine.

(Figure 30). Therefore, the pyridine moiety probably does not coordinate to 27. The shift in the potential of the second oxidation peak indicates that the pyridine moiety coordinates to either the one- or two-electron oxidation product to produce complexes of type 61, where m is equal to either 3 or 4. The coordination of the pyridine



$R = n\text{-C}_4\text{H}_9$

$X = \text{substituted pyridine}$

$m = 3, 4$

ligand in 61 is either relatively weak or occurs slowly relative to the voltammetric time scale when the substituted pyridines are very weak bases, such as 3- and 4-cyanopyridine. This is consistent with the fact that the couple centered at +0.60 V in Figure 22 (page 106) is virtually unchanged after scanning through the second oxidation wave in the presence of the weak bases (Figures 23 and 24).

The oxidation of 27 in the presence of substituted pyridines produced fairly well-defined reduction peaks at negative or small positive potentials for 4-benzoylpyridine, pyridine, 3,4-dimethylpyridine, and 4-dimethylaminopyridine as shown in Figures 25, 26, 28, and 29, respectively. These reduction peaks are due to products of the two electron oxidation of 27. This is demonstrated by the voltammograms of 27 in the presence of pyridine (Figure 31).

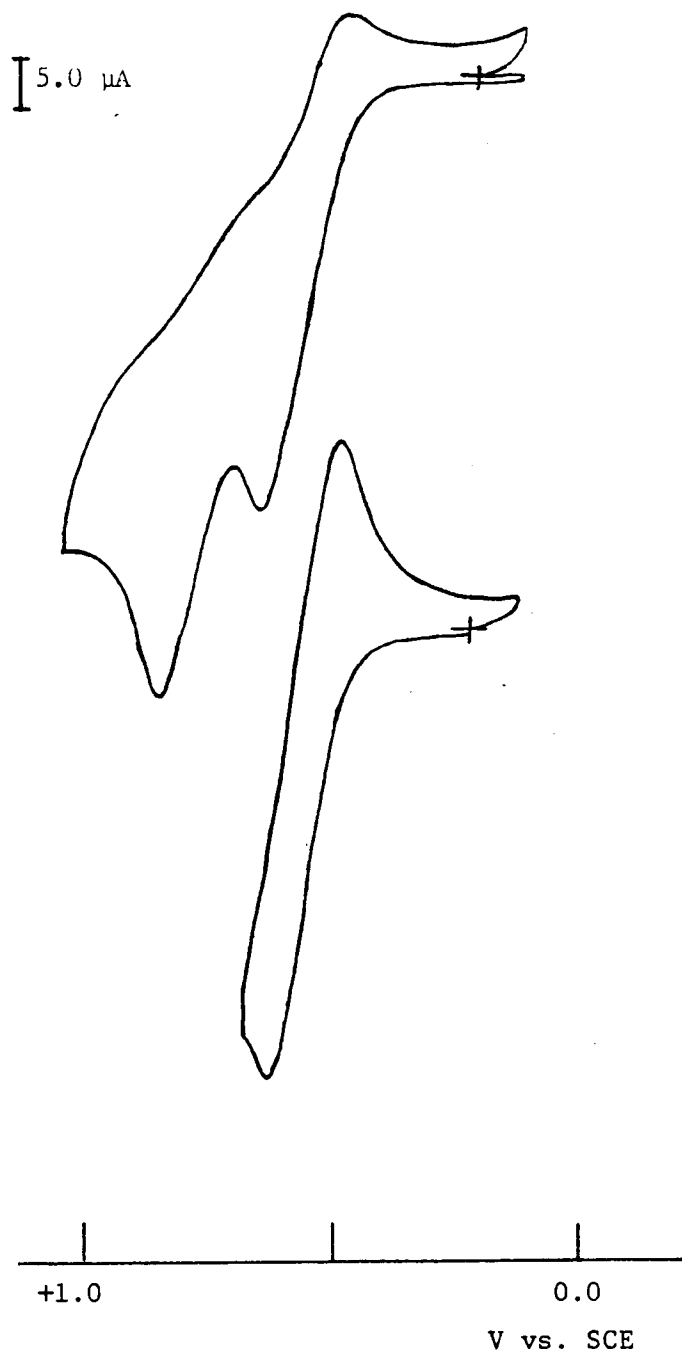


Figure 30. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\underline{n}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$, and 4×10^{-3} M pyridine.

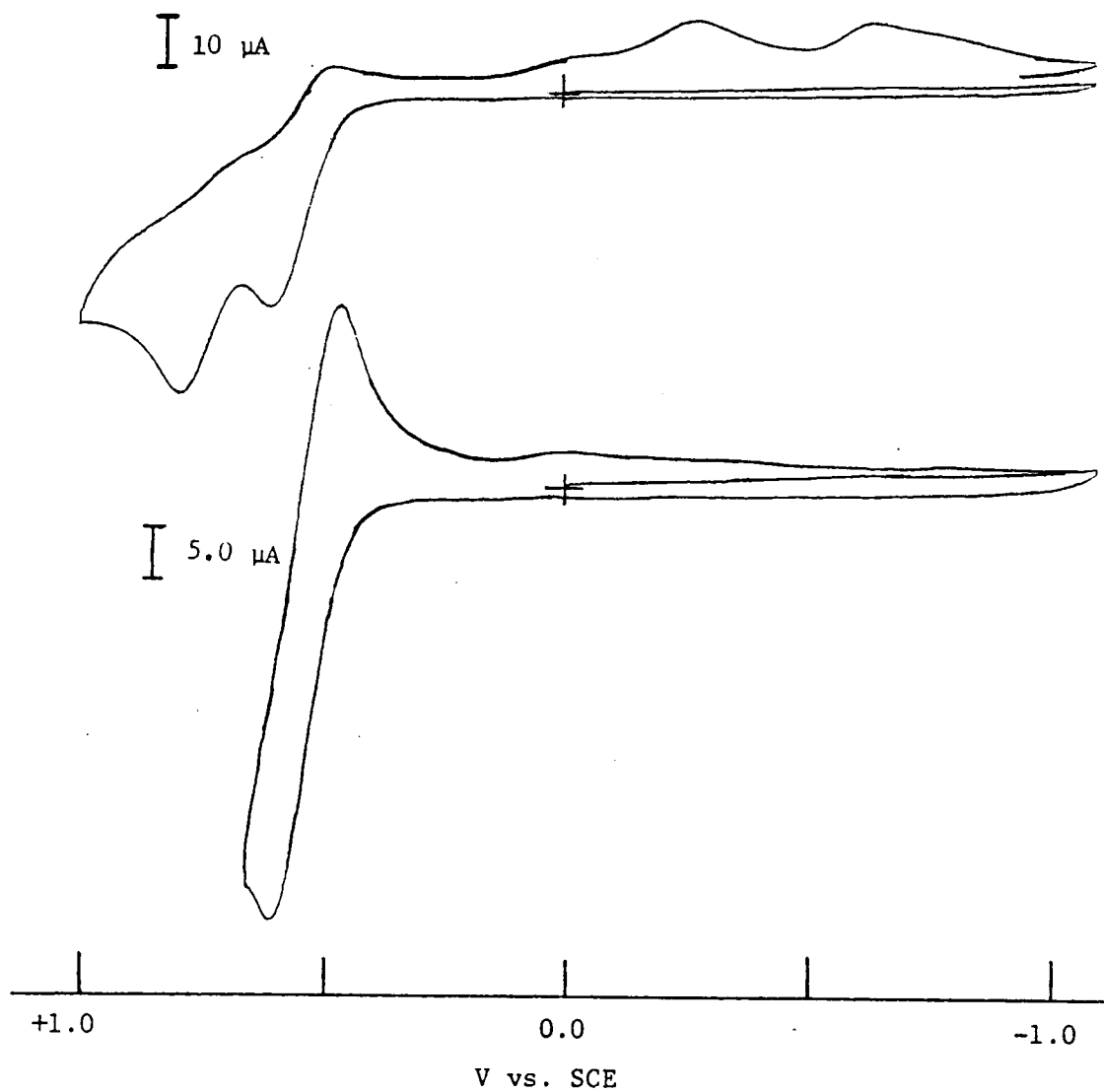


Figure 31. Cyclic voltammogram of 10^{-3} M $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in CH_2Cl_2 , 0.1 M $(\text{C}_4\text{H}_9\text{NPF}_6)$, and 4×10^{-3} M pyridine.

The general trend in the shift, ΔE , of the potential of the second oxidation peak of 27, when a given pyridine is added, is illustrated in Table VII. The basicities of the pyridines used are also given in Table VII. A plot of ΔE vs. the pK_b of the substituted pyridines is linear and is shown in Figure 32 (see Table VII). Every effort was made to maintain constant conditions under which the voltammograms in Figures 23-29 (pages 108, 110-115) were obtained. Even maintaining constant temperature and using the same stock solution, the initial voltammograms obtained before the addition of the substituted pyridines showed a slight variation in the shape and the potential of the second oxidation peak of 27. Shown in Figure 22 (page 106) is a representative voltammogram of 27 before the pyridine bases are added. The variations in the peak potential for the second oxidation wave are apparently caused by slight variations in the concentration of the rhodium complex. These variations in the peak shape and position caused some differences in the potential of the second oxidation wave for different solutions prior to the addition of the base. Therefore, each value for ΔE was calculated using the initial potential of the second oxidation peak for each solution.

The correlation between ΔE and the basicity of the coordinated pyridine may be explained by means of a simplified molecular orbital diagram (Figure 33). Although it is not known whether the pyridine ligand coordinates to the one-electron oxidation product or the two-electron oxidation product of 27 (or both), Figure 33 is based on the

TABLE VII

RELATIONSHIP BETWEEN ΔE FOR $[\text{Rh}_2(\text{n-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$
AND THE pk_b OF THE COORDINATING PYRIDINE

Substituent	pk_b	ΔE , V ^a
4-Me ₂ N(py)	4.29	0.565
3,4-Me ₂ (py)	7.39	0.476
4-Et(py)	7.98	0.460
py	8.77	0.400
4-benzoyl(py)	10.65	0.316
4-CN(py)	12.12	0.292
3-CN(py)	12.55	0.271

^a ΔE = the difference between the potential of the second oxidation wave of 27 in the presence of the base and the potential without the base present.

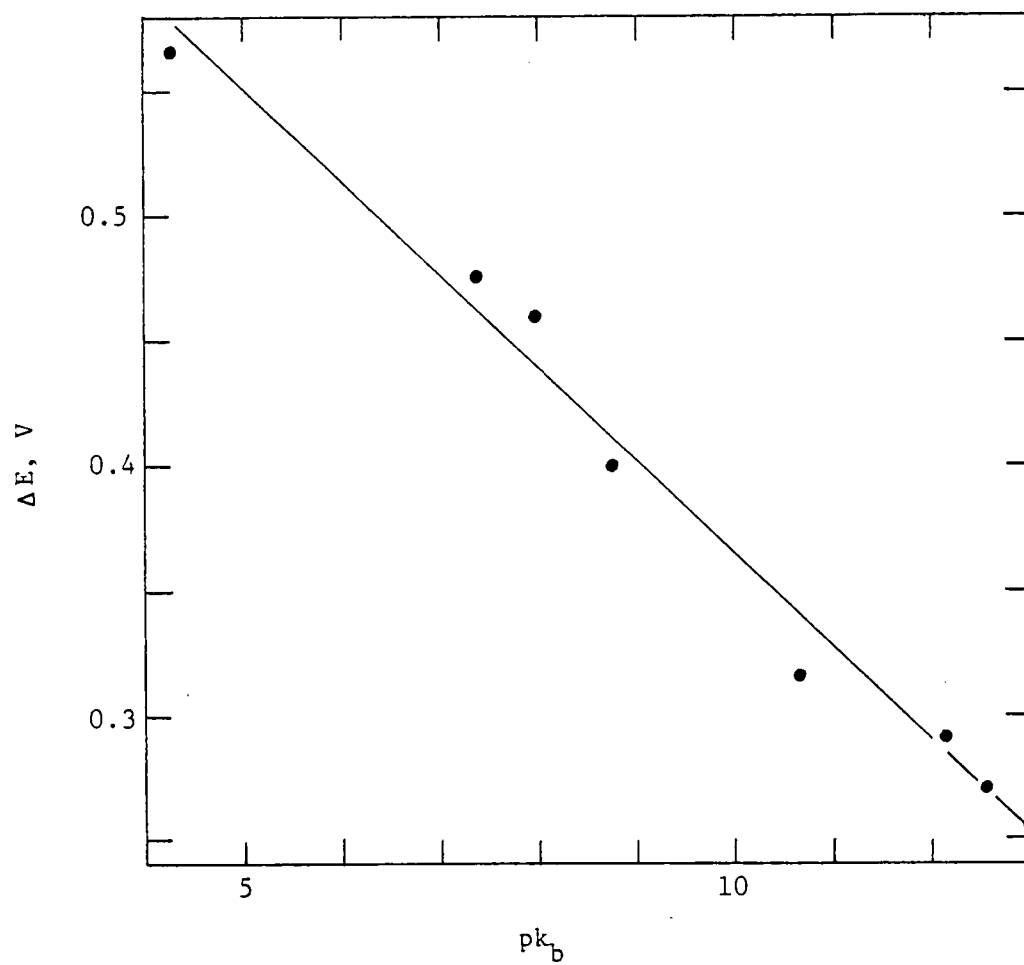


Figure 32. Plot of ΔE vs. pK_b for $[Rh_2(\underline{n}\text{-C}_4\text{H}_9\text{NC})_4(\text{DPM})_2](\text{PF}_6)_2$ in the presence of substituted pyridines.

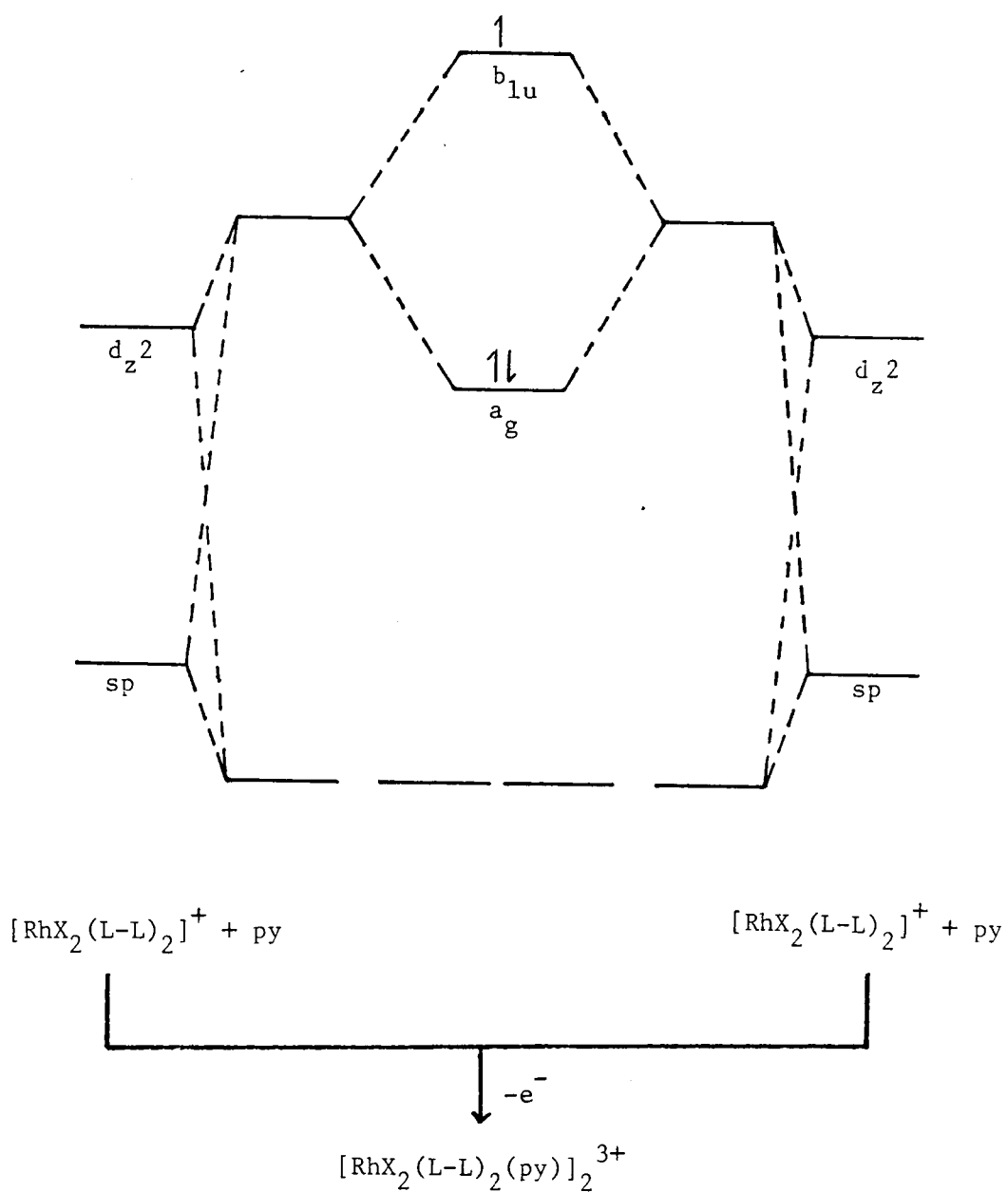


Figure 33. Simplified molecular orbital energy diagram for the coordination of substituted pyridines to binuclear rhodium complexes.

assumption that the pyridine species coordinates to the rhodium (1-1/2) center, in the $[\text{RhX}_2(\text{L-L})(\text{py})]_2^{3+}$ complex. If the actual coordination is to the rhodium(II) complex, a similar argument to the one discussed below can be made based on the stabilization of the final rhodium(II) complex upon coordination of the pyridine rather than the destabilization of the HOMO in the $[\text{RhX}_2(\text{L-L})_2(\text{py})]_2^{3+}$ complex.

Coordination of the pyridine to the rhodium (1-1/2) center is due to an interaction between the d_{z^2} rhodium orbital and the sp^2 lone pair orbital on the nitrogen. This interaction destabilizes the metal d_{z^2} orbital that produces the b_{1u} HOMO in the species $[\text{RhX}_2(\text{L-L})_2(\text{py})]_2^{3+}$ (Figure 33). This destabilization facilitates the removal of the electron from the b_{1u} orbital, thus shifting the second oxidation potential to less positive values in the presence of the base. As the basicity of the pyridine increases, the energy of the lone pair increases, shifting the energy of the donor σ orbitals closer to that of the metal d_{z^2} orbital. This better match in energy leads to greater interaction between the metal and ligand orbitals and thus a higher energy for the HOMO in the $[\text{RhX}_2(\text{L-L})_2(\text{py})]_2^{3+}$ species. As the pyridine base strength increases, the increased destabilization of the b_{1u} orbital results in easier removal of the second electron. Therefore, the second oxidation potential shifts to less positive values as the pyridine base strength increases, thus explaining the relationship between the pk_b of the base and ΔE .

CHAPTER VI

CONCLUSIONS

Although complexes of the type $[\text{Rh}_2(\text{RNC})_4(\text{DPM})_2](\text{PF}_6)_2$, 3, are capable of generating hydrogen from media containing water, it appears that a practical H_2 generating system involving these compounds is not possible due to their extremely short excited state lifetimes and the lack of a practical method of reducing the rhodium(II) species back to rhodium(I) species. The latter problem is compounded by a failure to characterize the photolysis and electrochemical oxidation products from systems containing chloride ions. These systems were expected to parallel the behavior of similar compounds reported in the literature, but they have not.

Electrochemical oxidation of compounds of type 3 have led to isolable complexes of the type $[\text{Rh}_2(\text{RNC})_4\text{L}_2(\text{DPM})_2]\text{X}_2$ ($\text{L} = \text{CN}^-$, SCN^- , and I^- ; $\text{X} = \text{PF}_6^-$, BF_4^-). It is of significant interest that these products with Cl^- occupying the transannular positions cannot be made by electrochemical, photolytic, or chemical oxidation of 3 in the presence of chloride ions, while complexes such as 5 readily undergo transannular addition of chloride ions. In non-coordinating media, two one-electron oxidation waves are observed for complexes of type 3 and the potential of the second oxidation peak of these complexes has been shown to be a function of the basicity of substituted pyridines added to the solution. Therefore, complexes of the type 3 are capable of coordinating to neutral as well as anionic ligands upon oxidation.

The differences in stability and structure shown by DAM, DPM, and DADPM complexes containing carbon monoxide and halide ligands are primarily due to differences in the rhodium-rhodium separations dictated by the varying bite sizes of the phosphine and arsine ligands. Small bridging groups such as carbon monoxide appear to be stable in the DPM complexes and decrease in stability in the order of $\text{DPM} > \text{DADPM} > \text{DAM}$ for these compounds. Further investigations of the differences in structures and reactivities of the DPM, DADPM, and DAM complexes as they apply to the catalytic capabilities of the complexes should be of great interest.

LIST OF REFERENCES

LIST OF REFERENCES

1. J. T. Mague and J. P. Mitchener, Inorg. Chem. 1969, 8, 119.
2. A. L. Balch, J. Am. Chem. Soc. 1976, 98, 8049.
3. J. T. Mague and S. H. DeVries, Inorg. Chem. 1980, 19, 3743.
4. M. Cowie and S. K. Dwight, Inorg. Chem. 1980, 19, 2500.
5. A. L. Blach, J. W. Labadie, and G. Delker, Inorg. Chem. 1979, 18, 1224.
6. W. A. Fordyce and G. A. Crosby, J. Am. Chem. Soc. 1982, 104, 985.
7. L. Malatesta and L. Vallarino, J. Chem. Soc. (London) 1956, 1867.
8. W. A. Fordyce, J. G. Brummer, and G. A. Crosby, J. Am. Chem. Soc. 1981, 103, 7061.
9. H. Isci and W. R. Mason, Inorg. Chem. 1975, 14, 913.
10. R. F. Dillinger, V. M. Miskowski, H. B. Gray, and W. H. Woodruff, J. Am. Chem. Soc. 1981, 103, 1595.
11. K. R. Mann, N. S. Lewis, R. M. Williams, H. B. Gray, and J. G. Gordon II, Inorg. Chem. 1978, 17, 828.
12. A. L. Balch, Ann. N. Y. Acad. Sci. 1978, 313, 651.
13. J. G. Gordon II, R. Williams, C.-H. Hsu, E. Cuellar, S. Samson, K. Mann, H. B. Gray, V. Hadek, and R. Samoano, Ann. N. Y. Acad. Sci. 1978, 313, 580.
14. A. L. Balch and M. M. Olmstead, J. Am. Chem. Soc. 1976, 98, 2354.
15. N. S. Lewis, K. R. Mann, J. G. Gordon II, and H. B. Gray, J. Am. Chem. Soc. 1976, 98, 7461.
16. Y. M. Miskowski, I. S. Sigal, K. R. Mann, H. B. Gray, S. J. Milder, G. S. Hammond, and P. R. Ryason, J. Am. Chem. Soc. 1979, 101, 4383.
17. I. S. Sigal and H. B. Gray, J. Am. Chem. Soc. 1981, 103, 2220.
18. A. L. Balch and B. Tulyathan, Inorg. Chem. 1977, 16, 2840.
19. A. R. Sangar, J. Chem. Soc. Chem. Comm. 1975, 893.

20. R. J. Haines, E. Meintjies, and Michael Laing, Inorg. Chem. Acta 1979, 36, L403.
=====
21. R. J. Haines and E. Meintjies, J. Chem. Soc. Dalton 1979, 367.
=====
22. V. M. Miskowskii, W. P. Schaefer, B. Sadeghi, B. D. Santarsiero, and H. B. Gray, Inorg. Chem. 1984, 23, 1154.
=====
23. T. Kawamura, K. Fukamachi, T. Towa, S. Hayashida, and T. Yonezawa, J. Am. Chem. Soc. 1981, 103, 364.
=====
24. R. Uson, L. A. Oro, D. Carmona, and M. Esteban, J. Organomet. Chem. 1981, 220, 103.
=====
25. R. Uson, L. A. Oro, M. A. Ciriano, M. T. Pinillos, A. Tiripicchio, and M. Tiripicchio Camellini, J. Organomet. Chem. 1981, 205, 247.
=====
26. J. P. Farr, M. M. Olmstead, and A. L. Balch, J. Am. Chem. Soc. 1980, 102, 6654.
=====
27. J. P. Farr, M. M. Olmstead, C. H. Hunt, and A. L. Balch, Inorg. Chem. 1981, 20, 1182.
=====
28. R. Appel, K. Geisler, and H. F. Scholer, Chem. Ber. 1979, 112, 648.
=====
29. P. D. Enlow and Clifton Woods, Organometallics 1982, 1, 886.
=====
30. M. Cowie, J. T. Mague, and A. R. Sangar, J. Am. Chem. Soc. 1978, 100, 3628
=====
31. C. P. Kubiak and R. Eisenberg, J. Am. Chem. Soc. 1977, 99, 6129.
=====
32. M. Cowie and S. K. Dwight, Inorg. Chem. 1980, 19, 2508.
=====
33. M. Cowie, Inorg. Chem. 1979, 18, 286.
=====
34. M. Cowie and S. K. Dwight, Inorg. Chem. 1980, 19, 2700.
=====
35. M. M. Olmstead, C. H. Lindsay, L. S. Benner, and A. L. Balch, J. Organometal. Chem. 1979, 179, 289.
=====
36. A. R. Sangar, J. Chem. Soc. Dalton 1981, 228.
=====
37. C. Woodcock and R. Eisenberg, Organometallics 1982, 1, 886.
=====

38. C. P. Kubiak and R. Eisenberg, J. Am. Chem. Soc. 1980, 102, 3637.
39. J. T. Mague and A. R. Sangar, Inorg. Chem. 1979, 18, 2060.
40. M. Cowie and S. K. Dwight, Inorg. Chem. Acta, 1978, 31, L407.
41. M. Cowie and T. G. Southern, Inorg. Chem. 1982, 21, 246.
42. M. Cowie and R. S. Dickson, Inorg. Chem. 1981, 20, 2682.
43. R. S. Dickson, S. H. Johnson, H. P. Kirsch, and D. J. Lloyd, Acta Crystallogr. 1977, B33, 2057.
44. R. S. Dickson, G. N. Pain, and M. F. MacKay, Acta Crystallogr. 1979, B35, 2321.
45. M. Cowie and T. G. Southern, J. Organomet. Chem. 1980, 193, C46.
46. E. L. Muetterties, Bull. Soc. Chim. Belg. 1976, 85, 451
47. E. L. Muetterties, W. R. Pretzer, M. G. Thomas, B. F. Beier, D. C. Thorn, V. W. Day, and A. G. Anderson, J. Am. Chem. Soc. 1978, 100, 2090.
48. R. S. Dickson and G. N. Pain, J. Chem. Soc. Chem. Comm. 1979, 277.
49. A. W. Maverick and H. B. Gray, Pure and Appl. Chem. 1980, 52, 2339.
50. K. R. Mann and H. B. Gray, Adv. Chem. Ser. 1979, 173, 225.
51. S.-F. Chan, M. Chou, C. Creutz, T. Matsbara, and N. Sutin, J. Am. Chem. Soc. 1981, 103, 369.
52. W. C. Trogler, D. K. Erwin, G. L. Geoffroy, and H. B. Gray, J. Am. Chem. Soc. 1978, 100, 1160.
53. P. K. Eidem, A. W. Maverick, and H. B. Gray, Inorg. Chem. Acta, 1981, 50, 59.
54. K. R. Mann, N. S. Lewis, V. M. Miskowski, D. K. Erwin, G. S. Hammond, and H. B. Gray, J. Am. Chem. Soc. 1977, 99, 5525.
55. K. R. Mann, M. J. DiPierro, T. P. Gill, J. Am. Chem. Soc. 1980, 102, 3965.

56. I. S. Sigal, K. R. Mann, and H. B. Gray, J. Am. Chem. Soc. 1980, 102, 7252. =====
57. J. T. Mague, Inorg. Chem. 1969, 8, 1975. =====
58. G. Giordano and R. H. Crabtree, Inorg. Syn. 1979, XIX, 218. =====
59. A. J. Gordon and R. A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References, (Wiley-Interscience) New York, N.Y., 1972.
60. R. J. Gale, B. Gilbert, and R. A. Osteryoung, Inorg. Chem. 1978, 17, 2728. =====
61. W. S. Woodward, R. D. Rocklin, and R. W. Murphy, Chem. Biomed. Environ. Instrum. 1979, 9, 95. =====
62. R. P. Van Duyne and C. N. Reilly, Anal. Chem. 1972, 44, 142. =====
63. J. O. Grimm and J. D. Mitchell, Inorg. Chem. 1979, 16, 1770. =====
64. P. Tinsley, M. S. Thesis, University of Tennessee, Knoxville, 1981.
65. D. R. Womack, private communication.
66. G. Brown, private communication.
67. H. B. Gray, K. R. Mann, N. S. Lewis, J. A. Thich, and R. M. Richmond, Adv. in Chem. Ser. 1978, 168, 45. =====
68. V. M. Miskowski, G. L. Nobinger, D. S. Kliger, G. S. Hamm, N. S. Lewis, K. R. Mann, and H. B. Gray, J. Am. Chem. Soc. 1978, 100, 485. =====
69. G. L. Geoffroy and M. S. Wrighton, Organometallic Photochemistry, (Academic Press) New York, N.Y., 1979.
70. M. S. Wrighton, ed., "Inorganic and Organometallic Photochemistry," Adv. Chem. Ser. 1978, 168. =====
71. K. R. Mann, R. A. Bell, and H. B. Gray, Inorg. Chem. 1979, 18, 2671. =====
72. M. Cowie and T. G. Southern, J. Organometal. Chem. 1980, 193, C46. =====
73. R. Colton, M. J. McCormick, and C. D. Pannan, J. Chem. Soc. Chem. Comm. 1977, 823. =====

74. R. Colton, M. J. McCormick, and C. D. Pannan, Aus. J. Chem. 1978, 31, 1425.
=====
75. M. P. Brown, A. N. Keith, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, and K. R. Seddon, Inorg. Chem. Acta 1979, 34, L223.
=====
76. M. Cowie and S. K. Dwight, Inorg. Chem. 1980, 19, 209.
=====
77. M. Cowie and S. K. Dwight, Inorg. Chem. 1981, 20, 1534.
=====
78. R. R. Guimerans and A. L. Balch, Inorg. Chem. Acta 1983, 77, L177.
=====
79. L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, (Wiley-Interscience) New York, N.Y., 1969.
80. J. D. Robinson, Inorg. Chem. Acta 1978, 27, L108.
=====
81. D. R. Womack, M.S. Thesis, University of Tennessee, Knoxville, 1981.
82. D.R. Womack, P. D. Enlow, and C. Woods, Inorg. Chem. 1983, 22, 2653.
=====
83. R. W. Murray and C. N. Reilley, Electroanalytical Principles, (Interscience), New York, N.Y., 1963.
84. D. H. Evans, K. M. O'Connell, R. A. Peterson, and M. J. Kelly, J. Chem. Ed. 1983, 60, 290.
=====
85. A. J. Bard, L. R. Faulkner, Electrochemical Methods Fundamentals and Applications, (John Wiley and Sons) New York, N.Y., 1980.
86. H. P. Boehm, Disc. Farad. 1971, 52, 264.
=====
87. H. Knozinger and P. Ratnasamy, Catal. Rev. Sci. Eng. 1978, 17, 31.
=====
88. A. Miezis, Acta Chem. Scand. 1973, 27, 3746.
=====
89. F. Basolo, J. L. Burmeister, and A. J. Poe, J. Am. Chem. Soc. 1963, 85, 1700.
=====
90. T. Ibusuki and Y. Saito, Inorg. Chem. Acta 1976, 19, 87.
=====
91. C. Daffron, M.S. Thesis, University of Tennessee, Knoxville, 1981.
92. C. McRobbie and H. Frye, Aust. J. Chem. 1972, 25, 893.
=====

93. J. A. Joule and F. G. Smith, Heterocyclic Chemistry, 2nd Ed. (Van Nostrand) New York, N.Y., 1978.
94. E. Klingsberg, ed., Pyridine and Its Derivatives, Part 2 (Interscience), New York, N.Y., 1961.
95. M. Taagepera, K. D. Summerhays, W. J. Here, R. D. Topson, A. Pross, L. Random, and R. W. Taft, J. Org. Chem. 1981, 46, 891.
96. I. Dzidic, J. Am. Chem. Soc. 1972, 94, 8333.
97. M. Taagerera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, J. Am. Chem. Soc. 1972, 94, 1369.
98. D. H. Aue, H. M. Webb, M. T. Bowers, C. L. Liotta, C. J. Alexander, and H. P. Hopkins, Jr., J. Am. Chem. Soc. 1976, 98, 854.
99. K. Schoefield, Hetero-aromatic Nitrogen Compounds (Plenum Press), New York, N.Y., 1967.

VITA

Paul Daniel Enlow, the third of three children, was born in Denver, Colorado on October 6, 1955. He graduated from Silver State Baptist High School, Lakewood, Colorado in June 1973. In June 1977 he was awarded a B.S. degree in Chemistry from Bob Jones University, Greenville, South Carolina. In August 1982 he was married to Christine Ann Erhart in Denver, Colorado. He was awarded a Ph.D. in Chemistry from The University of Tennessee, Knoxville, in August 1984.