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dissertation entitled Solvated Cations with Metal-Metal Bonds: Design Strategies and Reactivity of a New Class of Coordination Compounds

presented by

Laura Ellen Pence

has been accepted towards fulfillment of the requirements for

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SOLVATED CATIONS WITH METAL-METAL BONDS: DESIGN STRATEGIES AND REACTIVITY OF A NEW CLASS OF COORDINATION COMPOUNDS

By

Laura Ellen Pence

A DISSERTATION

submitted to Michigan State University in partial fulfillment of the requirement for the degree of

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1992

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ABSTRACT

SOLVATED CATIONS WITH METAL-METAL BONDS: DESIGN STRATEGIES AND REACTIVITY OF A NEW CLASS OF COORDINATION COMPOUNDS

By

Laura Ellen Pence

Historically, the use of starting materials possessing polar solvent moleties in one or more coordination sites has enhanced reactivity of transition metal species and allowed access to a variety of unusual molecules. The numerous advantages of acetonitrile over water as the labile solvent ligand include the reduced ability of the group to be transformed or act as a bridging group as well as the utility of these materials in organic media without decomposition. Homoleptic mononuclear acetonitrile species are known for roughly half of the transition elements, but prior to our research, easily accessible dinuclear examples were limited to only the dimolybdenum system. We proposed to further expand these examples by probing synthetic procedures to access dinuclear species in other metal systems. In addition, we sought to expand the chemistry of partially solvated systems such as $[M_2(OAc)_2(MeCN)_6]^{2+}$ (M = Mo, Rh).

Exploration of the reactivity of the partially solvated dirhodium cation, with a dimetal anion, $[n-Bu_4N]_2[Re_2Cl_8]$, precipitated the unusual soft salt, $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8](1)$ by metathesis rather than ligand

Laura Ellen Pence

redistribution or cation-anion annhilation occurring. This unusual structure suggests a wealth of reactivity for solvated dinuclear species.

Efforts to prepare fully solvated dinuclear species were very successful in the dirhodium system as both the [BF4]⁻ and [TFMS]⁻ salts of [Rh2(MeCN)₁₀]⁴⁺ were prepared as well as the [BF4]⁻ salt of the longer chain propionitrile species. The elementary reactivity of these species was established along with solvent exchange behavior in both nitriles and water. Spectroscopic studies revealed that the [Rh2(MeCN)₁₀][BF4]₄ salt displays reversible photochemistry with an extended lifetime before the original species is reformed. The versatility of this metal system indicates excellent potential for tailoring the starting material to various reaction conditions.

Elucidation of the general synthetic methodology to prepare solvated transition metal species had mixed success. The dinuclear chromium species is not produced in favor of the oxidized $[Cr(MeCN)_6]^{3+}$ species. Further investigation will be required in iridium, ruthenium and the extremely promising osmium chemistry to further generalized these preparative methods.

To my family, who always believed I could do anything I tried, and gave me the support and encouragement to make this dream come true.

My many mentors have set o attacen their environment and understanding when I needed it, some via electronic that also Dec. Correline and Don Dahlberg from LVC, and others in person like Gerry Bobesk and Am Estrison at MSU. A special size of appreciation goes to done Walls who found time for one during his own pursuit of tenure and schede to ton a research group. A brief word must be said for all the staff poppie who haded to work along. Many thanks go to Dec Ward for his Declars of the bring

i

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ii

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TABLE OF CONTENTS

Page

LIST	OF	TABLES		xv
LIST	OF	FIGURES		xviii
LIST	OF	ABBREVIA	TIONS	xxiii

CHAPTER I. 7 INTRODUCTION	1
Acetonitrile Versus Water in Coordination Complexes	2
Acetonitrile Binding Modes	8
Infrared Spectral Properties of Nitrile Complexes	9
Syntheses of Mononuclear Acetonitrile Compounds	13
Syntheses of Dinuclear Solvated Cations	18
LIST OF REFERENCES, CHAPTER I	23

CHAPTER II. CORREACTIONS OF PARTIALLY SOLVATED	
Malee CATIONS WITH A DIVALENT RHENIUM	
Reset ANION	27
A. Introduction	28
B. Experimental, Synthesis	30
(1) Synthesis of $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ (1)	
(i) Method 1	30
(ii) Method 2	31
(2) Reaction of [Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]	
in MeCN	31

(3) Reaction of [Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]	
in CH ₂ Cl ₂	32
(4) Reaction of [Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]	
in Acetone	32
(5) Reaction of [Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈] in THF	33
(6) Thermal Reaction of [Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]	
in the Solid State	33
(7) Work-up of Layer Reaction solutions	34
(8) Reaction of $[Rh_2(OAc)_2(MeCN)_6][BF_4]_2$ with	
Chloride ion	34
(9) Control reaction of [Re ₂ Cl ₈] ^{2.} with MeCN	35
C. Experimental, Crystallography	35
[Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]	35
D. Results and Discussion	38
Synthetic Methods	38
Spectroscopy	38
Molecular Structure	45
Reactions of [Rh2(OAc)2(MeCN)6][Re2Cl8]	58
E. Summary and Future Directions	63
IST OF REFERENCES, CHAPTER II	64
HAPTER III. SYNTHESIS AND REACTIVITY OF SOLVATED	
DIRHODIUM CATIONS	65
A. Introduction	66
B. Experimental, Synthesis	67
(1) Preparation of Rh ₂ (OAc) ₄ (MeCN) ₂	67

L

C

(2) Preparation of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ (2) 67
(i) Method 1 67
(18) B (ii) Method 2 68
(3) Metathesis of $[Rh_2(MeCN)_{10}][BF_4]_4$ with LiTFMS 69
(4) Metathesis of $[Rh_2(MeCN)_{10}][BF_4]_4$ with Sodium
tosylate
(5) Metathesis of $[Rh_2(MeCN)_{10}][BF_4]_4$ with
TBA(Tosyl)
(6) Preparation of [Rh ₂ (MeCN) ₁₀][TFMS] ₄ (3) 70
(7) Reaction of $[Rh_2(MeCN)_{10}][TFMS]_4$ with
(22) K Methanol
(8) Reaction of Rh ₂ (OAc) ₄ (MeOH) ₂ with HTFMS
220 C and Acetonitrile
(9) Reaction of Rh ₂ (OAc) ₄ (MeOH) ₂ with MeTFMS 72
(10) Reaction of [Rh2(MeCN)10][BF4]4 with
Propionitrile
(11) Synthesis of [Rh ₂ (EtCN) ₁₀][BF ₄] ₄ (4)
(12) Reaction of Rh ₂ (OAc) ₄ (MeOH) ₂ with HTFMS and
260 R Propionitrile
(13) Reaction of Rh ₂ (OAc) ₄ (MeCN) ₂ with Me ₃ SiTFMS and
270 R Propionitrile
(14) Reaction of Rh ₂ (OAc) ₄ (MeCN) ₂ with HBF ₄ and
Butyronitrile
(15) Reaction of $Rh_2(OAc)_4(MeCN)_2$ with Et_3OBF_4 and
Butyronitrile
(16) Reaction of [Rh ₂ (EtCN) ₁₀][BF ₄] ₄ with
Butyronitrile 75

(17) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with	
Benzonitrile	5
(18) Reaction of $[Rh_2(EtCN)_{10}][BF_4]_4$ with	
Benzonitrile 7	6
(19) Reaction of $Rh_2(OAc)_4(MeCN)_2$ with	
Pentanedinitrile 7	6
(20) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with	
Pentanedinitrile 7	6
(21) Reaction of $[Rh_2(MeCN)_{10}][TFMS]_4$ with	
Pentanedinitrile 7	6
(22) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with	
Propanedinitrile 7	7
(23) Conversion of $[Rh_2(MeCN)_{10}][BF_4]_4$ to	
Rh ₂ (OAc) ₄ (MeOH) ₂ 7	7
(24) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents	
of NaOAc7	8
(25) Reaction of $[Rh_2(MeCN)_{10}][TFMS]_4$ with	
2 equivalents of NaOAc 7	8
(26) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with	
NaO ₂ CCF ₃	8
(27) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ and	
NaO ₂ CC ₃ H ₇	9
(28) Reaction of $[Rh_2(EtCN)_{10}][BF_4]_4$ with 2 equivalents	
of [n-Bu ₄ N][OAc]	0
(29) Axial Substitution Reactions of $[Rh_2(MeCN)_{10}][BF_4]_4$	

(45) B (i) Reaction with MeOH 80
(ii) Reaction with THF
(iii) Reaction with Acetone
(30) Preparation of $Rh_2(aq)^{n+}$ (5)
(31) Crystallization attempt of Rh ₂ (aq) ⁴⁺
(32) Conversion of $Rh_2(aq)^{4+}$ to $Rh_2(OAc)_4$
(33) Aerobic Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with Water
at Room Temperature
(34) Reaction of $Rh_2(aq)^{n+}$ with Acetonitrile
(35) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with $HClO_4$
(36) Preparation of a UV-visible sample of $Rh_2(aq)^{n+1}$
in 3 <u>M</u> HClO ₄ 83
(37) Control reaction of Rh ₂ (OAc) ₄ (MeOH) ₂ in Water 83
(38) Reaction of $Rh_2(OAc)_4(MeOH)_2$ with Pyridine
and Et ₃ OBF ₄ 84
(39) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with Pyridine 84
(40) Reaction of $[Rh_2(MeCN)_{10}][TFMS]_4$ with Pyridine 84
(41) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents
of Bipyridine in Acetonitrile
(42) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents
of Bipyridine in Acetone
(43) Reaction of $[Rh_2(EtCN)_{10}][BF_4]_4$ with 2 equivalents
of Bipyridine
(44) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 4 equivalents
of Bipyridine

(45) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents	
Other of dppm	87
(46) Reaction of $[Rh_2(MeCN)_{10}][TFMS]_4$ with 2 equivalent	s
Axial of dppm	88
(47) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents	
of PMe3	88
(48) Reaction of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ with ppnCl	88
(49) Crystallization of an oxygen derivative of	
[Rh ₂ (MeCN) ₁₀][BF ₄] ₄	89
(50) Long term reaction of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄	
Chine with O2 and hy	89
Experimental, Crystallography	90
$= 1. \ [Rh_2(MeCN)_{10}][BF_4]_4 \ (2) \qquad \dots$	90
2. [Rh ₂ (MeCN) ₁₀][TFMS] ₄ (3)	90
3. $[Rh_2(EtCN)_{10}][BF_4]_4$ (4)	94
Results and Discussion	96
[Rh ₂ (MeCN) ₁₀][BF ₄] ₄	96
Experime Synthesis	96·
Spectroscopy	97
Molecular Structure	104
[Rh ₂ (MeCN) ₁₀][TFMS] ₄	111
Synthesis	111
Spectroscopy	113
Molecular Structure	114
[Rh ₂ (EtCN) ₁₀][BF ₄] ₄	123
Synthesis	123
Spectroscopy	126

C.

CHAID.

Molecular Structure	129
Other Nitriles	129
Carboxylate Reactions	142
Axial Substitution	143
Solvent Exchange, Rh ₂ (aq) ⁴⁺	146
Synthesis	146
Spectroscopy	146
Interconversions of the Rh ₂ ⁴⁺ core	149
Pyridine and Bipyridine Reactions	152
Tertiary Phosphine Reactions	153
Chloride Reactions	153
Oxygen Reactions	154
E. Summary	154
LIST OF REFERENCES, CHAPTER III	156
CHAPTER IV. PHOTOCHEMISTRY OF [Rh ₂ (MeCN) ₁₀][BF ₄] ₄	158
A. Introduction	159
B. Experimental, Synthesis	159
(1) Thermal Decomposition of $[Rh_2(MeCN)_{10}][BF_4]_4$	
in Solution	159
(2) Reduction of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ with the	
Tris(2,6-dimethoxyphenyl) Methyl Radical	159
(3) Reduction of $[Rh_2(MeCN)_{10}]^{4+}$ with	
Na-Acenaphthylenide (NaAce)	160
(4) Reduction of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ with	
Cobaltocene	161

(5) Reduction of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ with Cobaltocene	
in the presence of Electrolyte	161
(6) Crystallization attempt of the Cobaltocene reduction	
product	161
(7) Reduction of $[Rh_2(MeCN)_{10}][BF_4]_4$ by $NaEt_3BH$	162
(8) Bulk Electrochemical Synthesis of	
"[Rh4(MeCN)16][BF4]6"	162
(9) Electrocrystallization of [Rh ₄ (MeCN) ₁₆][BF ₄] ₆	163
(10) Reaction of $[RhCl(COD)]_2$ with $TlPF_6$	166
(11) Reaction of RhCl ₃ with TlPF ₆	166
(12) Reaction of RhCl ₃ with SbCl ₅	167
(13) Reaction of RhCl ₃ with AgBF ₄	167
(14) Reaction of RhCl ₃ with AgTFMS	168
(15) Synthesis of [RhCl ₂ (MeCN) ₄][BF ₄]	168
(16) Synthesis of [RhCl ₂ (MeCN) ₄][TFMS]	169
(17) Reaction of $[RhCl_2(MeCN)_4][BF_4]$ with	
[Na] ⁺ [mhp] [.]	169
(18) Reaction of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ with CO	
and light	170
(19) Aerobic reaction of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ with CO	
in the Presence of light	171
(20) Reaction of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ with CO	
in the dark	171
(21) Thermal reaction of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ with CO	
in the dark	172
(22) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 10 equivalents	
of <i>i</i> -PrNC	172

(23) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 10 equivalents
of n-BuNC 173
C. Experimental, Crystallography 174
[RhCl ₂ (NCCH ₃) ₄][BF ₄]
D. Results and Discussion 176
Electronic Spectroscopy of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ 179
Synthesis of Intermediates:
" $[Rh_4^{I,II,II,I}(MeCN)_{16}]^{6+}$ "
"[Rh ^I (MeCN) ₄]+"
"[Rh ^{III} (MeCN) ₆] ³⁺ "
Synthesis of $[RhCl_2(MeCN)_4]^+$ 192
Molecular Structure of [RhCl ₂ (MeCN) ₄][BF ₄] 196
Further Reactions with [RhCl ₂ (MeCN) ₄][BF ₄] 196
Photochemical Reactions of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄
with CO 203
Reactions with isocyanides
E. Summary
LIST OF REFERENCES, CHAPTER IV 206

CHAPTER V.	STRATEGIES FOR THE SYNTHESIS OF O	THER
	SOLVATED DINUCLEAR TRANSITION I	METAL
	COMPLEXES	208
A. Introd	uction	209
B. Exper	imental	211
(1)	Reaction of $Cr_2(OAc)_4 \cdot H_2O$ with Et_3OBF_4	211
(2)	Reaction of IrCl ₃ with TlPF ₆	211

	(3) Reaction of IrCl ₃ with SbCl ₅	212
	(4) Reaction of IrCl ₃ with AgBF ₄	212
	(5) Reaction of IrCl3 with AgTFMS	213
	(6) Reaction of IrCl ₃ with HBF ₄	214
	(7) Reaction of RuCl ₃ with TlPF ₆	214
	(8) Reaction of RuCl ₃ with AgBF ₄	215
	(9) Reaction of RuCl ₃ with HBF ₄	215
	(10) Reaction of RuCl ₃ with HTFMS	216
	(11) Reactions of anhydrous RuCl ₃	216
	(12) Reaction of $Ru_2(OAc)_2(CO)_4(MeCN)_2$	
	with Et ₃ OBF ₄	216
	(13) Reaction of $Ru_2(OAc)_4Cl$ with HBF_4	217
	(14) Reaction of Ru ₂ (OAc) ₄ Cl with HTFMS	217
	(15) Reaction of $[Ru_2(OAc)_4(THF)_2][BF_4]$ with HBF_4	217
	(16) Thermal reaction of [NH ₄] ₅ [Mo ₂ Cl ₉] with HBF ₄	218
	(17) Reaction of [NH ₄] ₅ [Mo ₂ Cl ₉] with HBF ₄ at Room	
	Temperature	218
	(18) Reaction of K ₄ [Mo ₂ Cl ₈] with HBF ₄	218
	(19) Reaction of $K_4[Mo_2Cl_8]$ with HTFMS in the presence	
	of Propionitrile	219
	(20) Reaction of Mo ₂ Cl ₄ (Me ₂ S) ₄ with HBF ₄	219
	(21) Reaction of K4[Mo2Cl8] with NaBPh4	219
10	(22) Reaction of OsCl ₃ and AgTFMS	220
	(23) Reaction of [n-Bu ₄ N] ₂ [Os ₂ Cl ₈] and HBF ₄	220
	(24) Reaction of $[n-Bu_4N]_2[Os_2Cl_8]$ with 8 equivalents	
	of AgBF ₄	220

(25) Reaction of $[n-Bu_4N]_2[Os_2Cl_8]$ with HTFMS in the	
presence of Propionitrile	221
(26) Reaction of Os ₂ (OAc) ₄ Cl ₂ with AgTFMS and	
Me ₃ SiTFMS	221
(27) Reaction of $Os_2(OAc)_4Cl_2$ with HBF_4 in the presence	
of Propionitrile	222
(28) Reaction of $Os_2(OAc)_4Cl_2$ with HBF_4 in the presence	
of Acetonitrile and Dichloromethane	222
C. Results and Discussion	224
Chromium	224
Iridium	232
Ruthenium	234
Molybdenum	239
Osmium	240
D. Summary	242
LIST OF REFERENCES, CHAPTER V	244
CHAPTER VI. CONCLUDING REMARKS AND FUTURE	-
DIRECTIONS	246
General	247
Mixed-Metal Cation-Anion reactions	247
Synthesis and Reactivity of Dirhodium Solvates	247
Photochemistry of [Rh ₂ (MeCN) ₁₀] ⁴⁺	248
Other Transition Metal Systems	248
Conclusions	252
LIST OF REFERENCES, CHAPTER VI	253
APPENDICES	254

A



LIST OF TABLES

		page
1.	Unit Cells of $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ determined at	
	different temperatures	36
2.	Crystal Data for [Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]	39
3.	Selected Bond Distances in Å for	
	[Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]	46
4.	Selected Bond Angles in degrees for	
	$[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$	48
5.	Crystal Data for [Rh ₂ (MeCN) ₁₀][BF ₄] ₄	91
6.	Crystal Data for [Rh ₂ (MeCN) ₁₀][TFMS] ₄	93
7.	Crystal Data for [Rh ₂ (EtCN) ₁₀][BF ₄] ₄	95
8.	Selected Bond Distances in Å for [Rh2(MeCN)10][BF4]4	105
9.	Selected Bond Angles in degrees for [Rh ₂ (MeCN) ₁₀][BF ₄] ₄	106
10.	Selected Bond Distances in Å for [Rh ₂ (MeCN) ₁₀][TFMS] ₄	117
11.	Selected Bond Angles in degrees for [Rh ₂ (MeCN) ₁₀][TFMS] ₄	118

12. Selected Bond Distances in Å for [Rh ₂ (EtCN) ₁₀][BF ₄] ₄ 13	0
13. Selected Bond Angles in degrees for [Rh ₂ (EtCN) ₁₀][BF ₄] ₄ 13	1
14. Summary of Spectral and Reactivity Properties for $Rh_2(aq)^{4+}$ 14	7
15. Crystal Data for [RhCl ₂ (MeCN) ₄][BF ₄]17	5
16. Selected Bond Distances in Å for [RhCl ₂ (MeCN) ₄][BF ₄] 19	7
17. Selected Bond Angles in degrees for [RhCl ₂ (MeCN) ₄][BF ₄] 19	8
18. Selected Bond Distances in Å for [Cr(MeCN) ₆][BF ₄] ₃	0
19. Selected Bond Angles in degrees for [Cr(MeCN) ₆][BF ₄] ₃	1
20. Atomic Positional Parameters (Å ²) and their estimated standard deviations for [Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]	6
 Atomic Positional Parameters (Å²) and their estimated standard deviations for [Rh₂(MeCN)₁₀][BF₄]₄	8
 Atomic Positional Parameters (Å²) and their estimated standard deviations for [Rh₂(MeCN)₁₀][TFMS]₄	0
 Atomic Positional Parameters (Å²) and their estimated standard deviations for [Rh₂(EtCN)₁₀][BF₄]₄	2

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ONTEP unit cell packing diagram for Eth 2 OAc(2 (McCN) c) (Pag Cls]

Schematic diagram of the unit cell of RhgfO.relg(MeCN)c.FRegCla1 showing the packing relasteriors of the Re-Re units. The singly labeled locations are units

LIST OF FIGURES

	Page
1.	Known homoleptic aqueous mononuclear and dinuclear
	transition metal cations
2.	Known homoleptic acetonitrile mononuclear and dinuclear
	transition metal cations
3.	Model of electron flow during nitrile stretching vibration.
	Upper white arrow represents flow of backbonding electrons from
	metal to ligand. Lower white arrow represents flow of electrons
	within ligand. Black arrow represents net electron flow.
	(Ref 14) 12
4.	Potential stacking configurations for the bridged and unbridged
	dimetal units 41
5.	Diagram of the dinuclear ionic components of
	[Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]
6.	ORTEP unit cell packing diagram for
	[Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]
7.	Schematic diagram of the unit cell of
	$[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ showing the packing orientation
	of the Re.Re units. The singly labeled locations are units

	parallel to the viewing angle. The Rh-Rh units are located in
	the empty boxes
8.	Representation of the three stacking modes of Re-Re units in the crystal, [Rh ₂ (OAc) ₂ (MeCN) ₆][Re ₂ Cl ₈]
9.	Qualitative electronic spectra of the kinetic and thermodynamic products of the reaction between [Rh2(OAc)2(MeCN)e][BF de and [mBu2N]2[Be2Cle1] (1) Solution
	from initial reaction in MeCN. (2) Kinetic salt in MeCN for 24 h. (3) Thermodynamic products(s) in MeCN
10.	¹ H NMR spectrum of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ recrystallized in the absence of light
11.	¹ H NMR spectrum of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ recrystallized in the presence of light
12.	ORTEP diagram of the cationic component of [Rh2(MeCN)10][BF4]4 viewed perpendicular to the Rh-Rh bond
13.	ORTEP diagram of the solvated cation of [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ viewed parallel to the Rh-Rh bond depicting the staggered nature of the molecule

14.	¹ H NMR of the orange form of [Rh ₂ (MeCN) ₁₀][TFMS] ₄	
	in CD ₃ NO ₂	116
15.	ORTEP packing diagram of [Rh2(MeCN)10][BF4]4. The anions	
	have been omitted for clarity	120
16.	ORTEP packing diagram of $[Rh_2(MeCN)_{10}][TFMS]_4$. The	
	anions have been omitted for clarity	122
17.	Space filling model of the dimetal cation in	
	[Rh ₂ (MeCN) ₁₀][BF ₄] ₄	125
18.	Cyclic voltammetry of (a) $[Rh_2(MeCN)_{10}][BF_4]_4$ and	
	(b) [Rh ₂ (EtCN) ₁₀][BF ₄] ₄	128
19.	ORTEP diagram of the dimetal cation in	
	[Rh ₂ (EtCN) ₁₀][BF ₄] ₄	133
20.	ORTEP packing diagram of [Rh2(EtCN)10][BF4]4. The	
	counterions have been omitted for clarity	135
21.	Space filling diagram of the cationic component of	
	[Rh ₂ (EtCN) ₁₀][BF ₄] ₄	137
22.	Diagram of the postulated staggered vs. eclipsed conformational	
	differences with monodentate and bidentate nitriles	140

23.	Comparison of the infrared spectra of the axial solvent	
	substition with [Rh ₂ (MeCN) ₁₀][BF ₄] ₄	145
24.	Interconversions of the [Rh ₂] ⁴⁺ core	151
25.	Diagram of a three compartment electrocrystallization cell	165
26.	Proposed mechanism for the reversible photochemistry of [Rh2(MeCN)10][BF4]4	178
27.	Electronic spectra of an anaerobically irradiated sample of $[Rh_2(MeCN)_{10}][BF_4]_4$ in MeCN solution recorded periodically	
	without additional exposure to light	181
28.	Electronic spectra displaying the thermal access to the Rh-Rh	
	bond cleavage reaction in [Rh ₂ (MeCN) ₁₀][BF ₄] ₄ in the absence of light	184
29.	Synthetic methods used to access the proposed mixed-valence tetramer, "[Rh4 ^{I,II,II,I} (MeCN) ₁₆] ⁴⁺ "	187
30.	Electronic spectrum of the proposed mixed-valence tetramer synthesized by bulk electrolysis redissolved in MeCN	189
31.	Cyclic voltammetry of a halide abstraction product with RhCl ₃ containing significant Ag ⁺ impurity, in Volts vs. Ag/AgCl	194

32.	ORTEP diagram of the cationic component of	
	[RhCl ₂ (MeCN) ₄][BF ₄]	200
33.	ORTEP unit cell packing diagram of [RhCl2(MeCN)4][BF4],	
	viewed down the A axis	202
34.	View of the discrete $Cr_2(OAc)_4L_2$ molecule and the extended	
	interaction in the anhydrous form. (Ref 13)	226
35.	Diagram of the crystallographically characterized	
	[Cr(MeCN) ₆] ³⁺	229
36.	Cyclic voltammetry of a halide abstraction product with IrCl ₃	
	containing significant Ag ⁺ impurity	236
37.	Diagram of a condenser and water trap to dehydrate reaction	
	solutions	251

minutes LIST OF ABBREVIATIONS

Âmol	angstrom
Ag/AgCl	silver-silver chloride reference electrode
nBu	n-butyl group
Calcd	calculated
cm ⁻¹	wavenumber
CV	cyclic voltammetry
d	deuterated
DMSO	dimethylsulfoxide
dppm	bis(diphenylphosphino)methane
e-	electron
ε	molar extinction coefficient
E _{1/2}	half-wave potential
EPR	electron paramagnetic resonance
EtCN	propionitrile
FT-IR	fourier transform infrared
g	grams
HBF ₄	tetrafluoroboric acid
HTFMS	trifluoromethanesulfonic acid
Hz	hertz
IR	infrared
M-M	metal-metal
Me	methyl group
MeCN	acetonitrile
mg	milligrams

mhp methylhydroxypyridine

min	minutes
ml	milliliters
mmol	millimoles
MSU	Michigan State University
nm	nanometer
NMR	nuclear magnetic resonance
obs	observed
OAc	acetate
ox	oxidation
ppn	bis(triphenylphosphoranylidene)ammonium
pTS	para-toluenesulfonate
Ph	phenyl group
red	reduction
sh	shoulder
TBAH	tetra-n-butylammonium hexafluorophosphate
TBABF4	tetra-n-butylammonium tetrafluoroborate
TFMS	trifluoromethanesulfonate
THF	tetrahydrofuran
TMPP	tris (2,4,6-trime thoxy phenyl) phosphine, P[C6H2 (OMe)3] 3
tolsyl	para-toluenesulfonate
V	volts

Acctemitrile Versus Waterin Constantion Comparison

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Unfortunately, the utility of agus species is somewhat limited by the difficulties of working in an aqueous medium. Many lights and condination compounds decompose in the presence of water and use achicontinue.² Additionally, water itself may undergo hydrolesis which all are

Acetonitrile Versus Water in Coordination Compounds

The ability of polar solvents to participate in metal ligation plays an important role in the synthesis of transition metal compounds. Common donor solvents such as water, nitriles, acetone, THF, pyridine, alcohols, and DMSO may be used to occupy otherwise vacant coordination sites on a metal center lending stability to the solution species, but promoting reactivity at the labile donor sites. This reduces the necessity for extreme reaction conditions or additional reagents to displace strong ligands, and allows reactions to be carried out under mild conditions and weaker donors to be added. The use of solvated starting materials often allows access to unusual compounds by avoiding undesirable thermal pathways. Examples are common in the early transition metals, for which it is customary to take advantage of partially solvated metal halide derivatives such as MCl₃(THF)₃, since these discrete mononuclear units react cleanly under mild conditions whereas the anhydrous polymeric halides tend to lead to disproportionation reactions.¹

Of the examples of fully solvated transition metal cations, by far the most widespread are the aqua complexes. Investigations of the syntheses and subsequent chemistry of these complexes span from the beginnings of inorganic coordination chemistry to the present. As indicated in Figure 1, these species are known for nearly all of the transition metals,² in fact, hydrated species of Mn, Fe, Ni, Cu, Ag, and Hg are commercially available.³

Unfortunately, the utility of aqua species is somewhat limited by the difficulties of working in an aqueous medium. Many ligands and coordination compounds decompose in the presence of water and are acid sensitive.² Additionally, water itself may undergo hydrolysis which alters

2



Figure 1. Known homoleptic aqueous mononuclear and dinuclear

transition metal cations

SeTiVCPMinFeCoNiCuZuYZuNbMisTcRuBinPdAgCdLeHfTaWReOsIrPtAuHg

recursors.6.7



mononuclear



dinuclear and mononuclear

Changing from an experience of one of the restriction of the restricti

its binding mode, coordination ability, and most likely the structure of the compound. Water is a strong donor in the aqueous medium and thus access to compounds containing weaker donors is reduced.

The use of nitriles as ligands offers an excellent alternative to water. Acetonitrile is a considerably weaker acid than water, and consequently a stronger base to maintain excellent donor ability while being far less likely to undergo decomposition under normal conditions.⁴ Furthermore, nitrile complexes are soluble in a variety of organic systems which reduces solvent self-exchange competition with an incoming ligand. Studies of the first row metals have established the relative solvent labilities as $\rm NH_3 > H_2O >$ $\rm CH_3CN > CH_3OH^5$ and although less labile than water, the ease of replacement of acetonitrile groups makes these complexes ideal synthetic precursors.^{6,7}

Methods of preparing these solvated compounds have varied widely and have included efforts with most of the common transition metal starting materials: metal halides, metal filings or powder, metal carbonyls, and hydrated metal salts. Examples of these homoleptic acetonitrile complexes are numerous, but not as widespread as the aqua analogs, as shown in Figure 2.

Changing from an aqueous to a nitrile ligand environment has the net effect of stabilizing lower oxidation states since the reducing nature of nitriles prevents these groups from supporting more highly charged metals.⁸ Redox changes also become less accessible in homoleptic acetonitrile complexes as illustrated by the $[Ru(NH_3)_5L]^{2+}$ system in which replacement of the one $L = H_2O$ ligand by acetonitrile leads to a stabilization of the +2 oxidation state by about 0.4 V.⁹ Although $[Ru(H_2O)_6]^{3+}$ may be

5



Figure 2. Known homoleptic acetonitrile mononuclear and dinuclear transition metal cations
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	Sc	ET.			Min	Fe	Co		Ca	Zn
10 N	Y	Zr	Nb	Mo	Тс	Ru	Rh	Pđ	Ag	Cd
10	La	Hf	Ta	w	Re	Os	Ir	Pt	Aa	Hg

mononuclear



dinuclear

pretra ha bee and it is a second card for any and the same brough X complexes.¹² has measured for a second for any any any to save brough X is created by the same of administry connected with a based of restance McCentra MCCHa). McCla² MCCHaidman's history of the same of a brought of a brought in the same of the easily prepared by oxidation of $[Ru(H_2O)_6]^{2+}$, there is no corresponding oxidation of the $[Ru(NCCH_3)_6]^{2+}$ species observed out to +2.5 V.¹⁰

Acetonitrile Binding Modes

The potential binding modes of alkyl nitriles are through the lone pair localized on the nitrogen atom (mode I, below), or through π donation from the C-N triple bond (mode II). In all but a few isolated examples, the bonding is of the former type.¹¹ The σ -bonded examples coordinate to the metal in a nearly linear fashion which has been crystallographically established (M-N=C angle close to 175 ± 5°) although significant deviations down to values of 160° have been observed.^{7,8} The N=C-R linkage maintains an angle much closer to linearity.



The shift to lower energies of the v(C=N) stretch in the infrared spectra has been used in the past to postulate side-on π -bonded nitrile complexes,¹² but unequivocal identification may only be made through Xray crystallography, since these bands have been correlated with σ -bonded groups as well.⁸ Examples of definitively characterized π -bonded species include MoCp₂(η^2 -NCCH₃), [MoCl(η^2 -NCCH₃)(dmpe)₂]⁺, (η^5 -C₅Me₅)(CO)Ir(η^2 -NCC₆H₄Cl), and a benzonitrile nickel clathrate compound, [(η^2 -C₆H₅CN)(PPh₃)Ni]₄.^{13a-d} In one isolated case, that of [W(bpy)(PMea)₂Cl(η^2 -NCCH₃)]⁺, structural and spectroscopic evidence supports the coordination of the nitrile as a four-electron donor.¹¹ The more common preference of nitriles for a σ -binding mode contrasts with the coordination flexibility of CO and adds to the greater lability of the solvent complexes.

Infrared Spectral Properties of Nitrile Complexes

The infrared spectral properties of acetonitrile complexes have been widely discussed.^{7,8,14,15} The CH₃CN molecule itself possesses C₃V symmetry and has eight normal modes of vibration, all of which are active in either the infrared or Raman spectra.^{16c} Four modes are totally symmetrical and belong to the species A₁, while four are degenerate and belong to the species E. The magnitude of the frequency shift upon coordination provides valuable information about the bonding interaction between the metal and the ligand. Unlike the negative shifts upon coordination of groups containing the moleties, C=O, P=O, and S=O which is due to a decrease in the force constant of the internal ligand bonding, coordinated nitriles usually display positive frequency shifts, concomitant with the increasing force constant of the stabilized C-N σ bond.⁷ This trend is general for nitriles coordinated to a Lewis acid via the nitrogen, although negative shifts for this mode are known.

The most diagnostic nitrile stretches are between 2200 and 2300 cm⁻¹ where few other groups are infrared active. Activity in this region is due to the v(C=N) stretch as well as a combination mode of the C-C stretch and a CH₃ deformation.^{16c} Differentiation between these two modes is easily made by comparing spectra of the CD₃CN adduct to the CH₃CN adduct.⁷ While the v(C=N) remains the same in both, the combination mode containing the CD₃ deformation experiences a shift due to the isotope effect.

9

Upon coordination to a metal, an additional IR active region for nitrile ligands is found in the far infrared where v(M-N) stretches occur. These strong modes, one for v(M-N) stretching and one for M-NCC wagging, usually fall in the range 330 and 180 cm⁻¹ in octahedral complexes, and are higher (450-230 cm⁻¹) in square planar species.^{16f} Incompletely substituted species may have values ranging from 100 cm⁻¹ for *trans*-PdX₂(NCPh)₂ (X = Cl, Br) to a maximum of 525 cm⁻¹ for $M(CO)_3(NCCH_3)_3$ (M = Cr, Mo, W).⁷ Specific assignment of modes to bands in the far infrared is often complicated due to the symmetry interactions of the ligand and metal-ligand modes, and the additional modes from the ligands or counterions in this region.

It has been noted by Johnson and Taube¹⁴ that the observed infrared intensity of the v(C=N) bands does not necessarily correlate with the presence or number of nitrile ligands; in some cases the anticipated bands are totally absent. There are major categories of metal-nitrile interactions that give rise to differences in v(C=N)intensitites. In metal ions that lend themselves well to back-bonding interactions, such as Ru(II) and Os(II), this leads to net electron flow from the metal to the ligand generating a dipole with a positive charge on the metal and a negative charge on the ligand which enhances the intensity. In cases where there is little or no π back-bonding, the net electron flow from the ligand to the metal through the sigma bond predominates and the intensity is no longer enhanced by the metal-ligand dipole. In intermediate cases, the ligand σ and metal π backbonding electron flows are approximately equal, canceling any dipole moment of the infrared mode and significantly reducing or eliminating the intensity of the stretching mode. This situation is depicted in Figure 3. (a) Weak back bedan to a life the life ball of

Figure 3. Model of electron flow during nitrile stretching vibration. Upper white arrow represents the flow of backbonding electrons from metal to ligand. Lower white arrow represents the flow of electrons within ligand. Black arrow represents net electron flow. (Ref 14)

c) Strong back bonding Ro(II), OstF

Figure 3



(a) Weak back-bonding: Co(III), Rh(III), Ru(III)



incorporate (b) Intermediate back-bonding: Os(III), Ir(III)



nd Cd were all prep

Syntheses of Mononuclear Acetonitrile Compounds

The most comprehensive studies of acetonitrile compounds were carried out by Groeneveld and coworkers in the mid 1960's.¹⁶ Since this was prior to widespread use of X-ray crystallography, these complexes were characterized primarily by elemental analysis, infrared spectroscopy, and magnetic susceptibility measurements. The limitations of these methods for allowing differentiation between coordinated and interstitial solvent prompted researchers to propose several stoichiometries for a single oxidation state of several of the transition metals. The correct formulations were subsequently identified by other research groups, and reliable stoichiometries were eventually established in questionable cases.

The principal synthetic strategy for these numerous studies involved reactions of metal halides and with a halide abstraction reagent that incorporates the liberated chloride into the counterion as exemplified by the equation outlined below:

 $\frac{MCl_x + x \text{ SbCl}_5}{MCl_x + x \text{ SbCl}_5} \xrightarrow{\text{CH}_3\text{CN}} [M(\text{NCCH}_3)_n][\text{SbCl}_6]_x$ (x = 1-3, n = 2,4, or 6)Equation 1

Antimony pentachloride proved to be an excellent reagent in the more easily handled form, SbCl₅ · CH₃CN, and monovalent complexes of Li, Na, K, Rb, Cs, Ag, Au and Tl as well as divalent species of Be, Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pd and Cd were all prepared by reaction with the appropriate metal halide in acetonitrile. ^{16a} Trivalent species accessed by this method include solvated compounds of Al, Ga, In, Cr, V, and La.^{16d} In the latter cases, potentiometric titrations supported the formulation of

13

each as fully solvated despite the increasing metal charge and number of halides in the starting material which might be expected to retard or even prevent the transfer of chloride ions. Reactions of TiCl₂, VCl₂, and CrCl₂ with SbCl₅ under the same conditions led to oxidation of the metal; no complex could be isolated from the reaction with HgCl₂. Incomplete halide transfer resulted from the reaction between FeCl₃ and SbCl₅.

The halide abstraction reagent, tetrachlorotin(IV) is also conveniently handled as the acetonitrile solvate, SnCl₄ · 3 CH₃CN. Complexes of [SnCl₆]²⁻ have been isolated for Li⁺, Na⁺, Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu⁺, and Cu^{2+,16b} although the existence of identical Cu species in two different oxidation states seems unlikely. Solvated species of K, Rb, Cs, and Tl were not accessible by this method leading to the conclusion that SnCl₄ is a weaker halide abstraction reagent than SbCl₅. Extrapolation of this general extraction and incorporation method was provided by the reagents BCl₃, AlCl₃, GaCl₃, InCl₃, TlCl₃, and FeCl₃ with the divalent cations of Be, Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Hg, and Pd.^{16e,h,i,j} These agents were ranked in order of chloride acceptor ability to be:

TlCl₃ > SbCl₅ > FeCl₃ > GaCl₃ > InCl₃ > AlCl₃ > SnCl₄ > BCl₃

This general methodology has been explored by other researchers since the early work of Groeneveld and coworkers. Several groups have independently verified this general methodology for SbCl₅ with V and Cr,¹⁷ Zn,¹⁸ and Ni.¹⁹ An unusual halide incorporation reaction was reported by Wilkinson and coworkers involving the reaction of VCl₃ and ZnEt₂. Halide abstraction was accompanied by a reduction of the vanadium from III to II to yield the product [V(MeCN)6][ZnCl4].²⁰

The strategy of sequestering the liberated halide in the counterion has certainly been an extremely successful method of preparing salts of acetonitrile cations, but difficulties arise from the relatively reactive nature of the halide containing counterions. It has been noted in some cases, that anions such as [SbCl6]⁻ and [SnCl6]²⁻ interfere with subsequent chemistry, often by releasing halides back into the system. Thus total removal of the abstracted Cl⁻ ligand and substitution for a more innocuous anion would be preferred. The use of silver or thallium salts as halide abstraction reagents are viable alternatives, since the removed ligand is precipitated as TICl or AgCl and may be separated from the product by filtration as indicated in the equation below. Reports of this halide sequestering and removal

 $\frac{MCl_x + x AgBF_4}{MCl_x + x AgBF_4} \xrightarrow{CH_3CN} [M(NCCH_3)_n][BF_6]_x + X AgCl (s)$ $(x = 1 \cdot 3, n = 4 \text{ or } 6)$ Equation 2

method are not as widespread as for halide abstraction and incorporation into the anion, but it has been shown that the $[Pt(NCCH_3)_4][BF_4]_2$ species is easily prepared by the action of AgBF4 on PtCl₂(NCCH₃)₂,²¹ and $[Co(NCCH_3)_6][PF_6]_2$ is cleanly isolated from the reaction of CoCl₂ and AgPF₆,²²

A strategy for preparing fully solvated acetonitrile cations that was elucidated even before the metal halide investigations (*vide supra*), is that of using metal filings or powder and an oxidant such as NOBF₄ or NOClO₄ in CH₃CN medium. These reactions yield solvated solids originally

15

formulated as $M(BF_4)_2 \cdot 4 CH_3CN$ for M = Cu, Mn, and Zn, and $M(BF_4)_2 \cdot 6 CH_3CN$ for M = Ni, Fe, Co.²³ This approach was later extended to other metal systems by Sen and coworkers for the syntheses of $[Pd(NCCH_3)_4][BF_4]_2$,²⁴ and $[Eu(NCCH_3)_3(BF_4)_3]_x^{25}$ according to the following equation:

 $M(s) + x \text{ NOBF}_4 \xrightarrow{\text{CH}_3\text{CN}} [M(\text{NCCH}_3)_n][\text{BF}_4]_x + X \text{ NO} (g)$ $(x = 1 \cdot 3, n = 4 \text{ or } 6)$ Equation 3

Direct preparation of solvated species by electrochemical methods was reported for [Au(NCCH₃)₂]⁺ which involves anodic dissolution of the metal in acetonitrile.²⁶ Addition of HBF₄ to the CH₃CN system was required for the electrochemical oxidation of Ti and Cr metals to [Ti(NCCH₃)₆][BF₄]₃ and [Cr(NCCH₃)₆][BF₄]₂.²⁷ The In³⁺ species was also prepared in these experiments. This experiment represents the only report of a Cr²⁺ system; other results indicate that the Cr³⁺ species is preferred.^{16d,17}

Metal oxides are occasionally used for the synthesis of mononuclear acetonitrile cations. Dissolution of Cu₂O in CH₃CN and 2 <u>M</u> HClO₄ at 100 °C deposits colorless crystals of [Cu(NCCH₃)₄][ClO₄] upon cooling. ²⁸ An excess of MnO₂ treated with aqueous HClO₄ and 30% H₂O₂ gives the aqueous solvate which may be dehydrated with molecular sieves in a Soxhlet extractor in the presence of acetonitrile to yield [Mn(NCCH₃)₆][ClO₄]₂.²⁹ The conversion of hydrated iron perchlorate to [Fe(NCCH₃₎₆]²⁺ may also be easily effected by this CH₃CN / molecular sieve debydration method.⁵

Finally, synthesis of a few metal acetonitrile species is even more straightforward. Recrystallization of $[Ru(H_2O)_6][TFMS]$ from acetonitrile cleanly produces the CH₃CN solvated species.¹⁰ The same simple procedure is used to obtain crystals of $[Ag(NCCH_3)_4][ClO_4]^{30}$ and samples of the Mn²⁺, Fe²⁺, and Co²⁺ perchlorate salts.³¹

In some instances, fully solvated species form serendipitously from other reaction strategies. For instance, the interaction of *trans*-[V(NCCH₃)₂(dmpe)₂][BPh₄]₂ with HCPh(SO₂CF₃)₂ produces [V(NCCH₃)₆][BPh₄]₂ in low yield.^{13b} It is apparent that the action of the acid protonates the phosphine ligands which are good leaving groups, but this was not a particularly direct or intuitive method of synthesis. An even more unusual result occurred in the reaction between [{Ru(η⁶-C₆Me₆)Cl₂]₂] and [NEt₄]₂[B₁₀H₁₄] in CH₃CN solution to give a high yield of [Ru(NCCH₃)₆][7-(η⁶-C₆Me₆)-*nido*-7-RuB₁₀H₁₃]₂.³² Both of these species have been reported by other methods as well.^{10,20}

Considering that the main body of the solvated transition metal chemistry was carried out in the early 1960's, many of these species have not had the benefit of modern methods of characterization. Subsequent investigations have led to numerous examples characterized by X-ray diffraction. These include Ni(II),^{19,33} Ru(II),³² V(II),²⁰ Fe(II),^{34,35} Cu(I),²⁸ and Ag(I),³⁰ Powder diffraction data indicate that the Mg(II) and Ni(II) complexes are isostructural with Fe^{2+,34}

Mononuclear carbonyls of the form, M(CO)₆, are another common starting material for solvated species. Unlike the aforementioned reactions, this source does not appear to yield homoleptic solvent products. For Cr, Mo, and W, a procedure involving refluxing the metal carbonyl in acetonitrile removes three carbonyls in a facial arrangement to yield partially solvated species of the form, fac-M(CO)₃(NCCH₃)₃.³⁶ The analogous Re complex was prepared unexpectedly by a different synthetic route. The reaction of [n-Bu₄N]₂[Re₄(CO)₁₆] with AgBF₄ in CH₃CN unexpectedly deposits silver metal and yields [Re(CO)₃(NCCH₃)₃][BF₄] in another example of serendipitous formation of a solvated species.³⁷

Chemical oxidation of the metal carbonyls of molybdenum and tungsten with NOBF₄ removes all the carbonyl ligands, but produces nitrosyl species of the form, [M(NO)₂(NCCH₃)₄][BF₄]₂ for M=Mo, W.²⁴ Coordination of the NO by-product prevents one from using this route to access fully solvated species for these metals. Compounds of this general type also exist for Rh. The reaction of NOBF₄ with [Rh(COD)(NCCH₃)₂][X] or [Rh(COD)₂][X] (COD = 1,5-cyclooctadiene) in acetonitrile yields [Rh(NCCH₃)₄(NO)][X]₂.³⁸

Syntheses of Dinuclear Solvated Cations

Although numerous examples of mononuclear acetonitrile and aqua solvated species have been prepared, dinuclear complexes are rare. When our research commenced, three solvated dinuclear species were known for only two metals: the aqua cations of $Mo_2^{II,II}$ and $Rh_2^{II,II}$, and the acetonitrile species for $Mo_2^{II,II}$.

The dinuclear rhodium aquo complex was reported by Taube and coworkers from the reduction reaction: ³⁹

 $2 [Rh(H_2O)_5Cl]^{2+} + 2 [Cr(H_2O)_6]^{2+} \longrightarrow [Rh_2(H_2O)_{10}]^{4+} + 2 [Cr(H_2O)_5Cl]^{2+}$

Equation 4

The resulting charged species were separated on a cation-exchange column. The Cr containing fraction was eluted by 1 <u>M</u> HClO₄ while the more highly charged Rh_2^{4+} complex was removed with 3 <u>M</u> HClO₄. Other Rh(III) starting materials, $[Rh(H_2O)_6]^{3+}$ and $[Rh(H_2O)_5Br]^{2+}$ were later found to yield the same products and a slight reduction of the acid concentration was possible.^{39b} Unfortunately, the constraints of the acidic medium prevented a solid from being obtained without decomposition of the compound.

Wilkinson and coworkers subsequently reported synthesis of the same species by an alternative route:⁴⁰

$$Rh_2(OAc)_4 + 4 HBF_4 \longrightarrow Rh_2^{4+} + 4 BF_4^- + 4 HOAc$$

Equation 5

The Taube group found some disparities between these reports and their original work and proceeded to reproduce the reaction conditions reported by Wilkinson. Their experiments suggested that protonation of the acetates is incomplete in the above reaction leaving behind two or three bridging. groups on the dirhodium unit. Taube's conclusions were advanced on the premise of the difference in the cation exchange behavior of the Wilkinson species which eluted at much lower acid concentration and the lack of decomposition of the solutions upon reduction of the volume.⁴¹ These observations were in direct contrast to the properties of the "authentic" Rh₂(aq)⁴⁺ prepared from the reduction of Rh(III) complexes. Because of the unresolved controversy regarding the acetate method, preparation from the mononuclear Rh(III) species remains the only unquestionable method of synthesis for the $Rh_2(aq)^{4+}$; unfortunately the highly acidic medium restricts exploration of subsequent chemistry.⁴²

Several, largely unsuccessful, attempts to prepare $Mo_2^{4+}(aq)$ from the same route as the Rh synthesis, namely the reduction of $MoCl^{2+}$ with Cr^{2+} were reported by Taube and coworkers.⁴³ A different strategy was then employed, borrowing from the mononuclear examples to acidify the chlorides of K₄Mo₂Cl₈ · 2 H₂O with 0.25 <u>M</u> HTFMS. This appeared to be successful, but isolation of the pure aqua material was not possible. The

$$K_{4}Mo_{2}Cl_{8} + HTFMS \xrightarrow{MeCN} [Mo_{2}(aq)][TFMS]_{4} + 4 KTFMS + 8 HCl (g)$$

Equation 6

red compound was strongly retained by cation-exchange resins to eluent concentrations of 1 <u>M</u> HTFMS. A more highly charged anion was used in the form of 3 <u>M</u> H₂SO₄ which leads to derivatization of the Mo₂^{II,II} unit to give K₄[Mo₂(SO₄)₄].⁴³ Barium triflate solutions may be used to convert this sulfate species to the molybdenum(II) water compound, but no solid can be isolated; furthermore the solutions are stable for only hours under N₂ before decomposition ensues.⁴⁴

Preparation of the dinuclear Mo(II) species of acetonitrile was first reported by a two step synthesis from Mo₂(O₂CH)₄.⁴⁵ The formate was refluxed with HTFMS and trifluoromethanesulfonic anhydride to form the very moisture sensitive compound, $[Mo_2(H_2O)_4(TFMS)_2][TFMS]_2$. This solid was then dissolved in acetonitrile with reduction of the volume and chilling to produce blue crystals of " $[Mo_2(NCCH_3)_8][TFMS]_4$ ". The species, $Mo_2(TFMS)_4$ had earlier been prepared by action of HTFMS on $Mo_2(OAc)_4$ in the same laboratory,⁴⁶ but the product was reported to be extremely difficult to separate from an acetate impurity. Use of the formate takes advantage of this ligand's decomposition in strong acid to carbon monoxide and water. The acetonitrile species is insoluble in non-polar solvents and reacts with coordinating solvents. It easily reverts back to $Mo_2(OAc)_4$ upon reaction with acetic acid. The species formulated as " $[Mo_2(NCCH_3)_8]^{4+"}$ by Abbott is very air sensitive and apparently loses solvent readily under vacuum. Crystals were finally grown at a much later date by Cotton and coworkers.⁴⁷ The compound was identified as $[Mo_2(NCCH_3)_{10}]^{4+}$ in the form of the $[BF_4]^-$ salt, indicating that solvent is present in the axial positions contrary to the original formulation.

Finally, during the course of the research reported in this thesis, Baranovskii and coworkers reported the synthesis of $[Rh_2(NCCH_3)_8(H_2O)_2][PF_6]_4$ from either rhodium(II) acetate or $Na_4[Rh_2(SO_4)_4(H_2O)_2]$ through the action of trifluoromethanesulfonic acid.⁴⁸ Recrystallization of the initial product in the presence of NaPF₆ gave the $[Rh_2(NCCH_3)_8(H_2O)_2][PF_6]_4$ salt. X-ray characterization and further reactivity studies had not been carried out before our studies were reported.⁴⁹ A detailed investigation of other methods of synthesis and the elementary reactivity of the compound would prove quite advantageous to future work.

The paucity of dinuclear solvated complexes and their potential usefulness led us to explore the designed synthesis of other examples of these cations. Primarily, we wished to establish general methods of preparation to access these species, especially considering the problematic syntheses described by others. Successful strategies beginning from the mononuclear investigations may be applied when possible, but it is realized that dinuclear species may not necessarily be prepared conveniently

21

through these routes. The possibility of using starting materials for dinuclear species such as the carboxylates broadens the potential techniques for producing different metal analogs. The broad goal of the research described in this thesis was to investigate, in a general manner, the possible methods for accessing various $[M_2(NCCH_3)_x]^{n+}$ species. In addition, the full characterization and solution chemistry of these systems was targeted.

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CHAPTER II

REACTIONS OF PARTIALLY SOLVATED CATIONS WITH TRANSITION METAL ANIONS

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A. Introduction

In the mid 1980's, two groups independently reported the partially solvated acetonitrile species of the form, $[M_2(OAc)_2(MeCN)_6]^{2+}$ for M = Rh, Mo, 1 prepared under mild conditions by the action of Et_3OBF_4 on the tetracarboxylates, $M_2(OAc)_4$. The structure, as shown below,



possesses two bridging carboxylates in a *cis* disposition to each other with coordinating solvent occupying the other four equatorial sites and the two axial sites. The axial ligands exhibit longer M-N distances than the equatorial groups, indicating these solvent molecules are less tightly held. This is easily explained by the *trans* influence of the M-M bond.

The ligand distribution in these cations presents an unusual case wherein one side of the molecule is stabilized by anionic bridging groups while the other side, which possesses more labile neutral groups, is open for reactivity. The equatorial solvent molecules bound to the molybdenum species are actually substantially more labile than those of the rhodium system, as evidenced by ¹H NMR spectroscopy. The MeCN ligands on the $[Mo_2]^{2+}$ unit rapidly exchange for deuterated solvent to give only a singlet in the ¹H NMR spectrum due to free uncoordinated solvent. ^{1c} The $[Rh_2]^{2+}$ system displays two discrete MeCN resonances in the 2:1 ratio dictated by the presence of four coordinated equatorial ligands and two free MeCN ligands lost from the axial positions due to exchange with CD_3CN .^{1c} This lability difference between dimetal units is not restricted to solvent ligands. For M=Mo, rapid scrambling of carboxylates between molecules occurs in the reaction of $M_2(O_2CR)_4$ and $M_2(O_2CR')_4$, while no such process is observed for M=Rh.²

Chisholm and Cayton, in some recently published work, proposed this difference in lability to be related to the difference in the M-M molecular orbital configuration.² The Mo-Mo tetra-cation has a configuration of $\sigma^2 \pi^4 \delta^2$ with low-lying, empty δ^* and π^* orbitals localized on the metal centers which allows ligand exchange to take place via an associative mechanism. By contrast, the Rh-Rh single bond possesses an electron rich $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*4}$ configuration which effectively shuts down the associative mechanism and makes the equatorial sites relatively inert, similar to the octahedral t_{2g}^6 ML₆ complexes whose reactivity is very slow.

The reactivity of $[Mo_2(OAc)_2(MeCN)_6]^{2+}$ has not been extensively investigated. The reaction of this species with the bidentate ligand, dmpe, (dmpe = 1,2-dimethylphosphinoethane) results in the displacement of four solvent ligands with concomitant isomerization to the *trans* compound, $[Mo_2(OAc)_2(dmpe)_2][BF_4]_2.^3$ Tridentate donors such as the macrocyclic thioether, 1,4,7-trithiacyclonone (TTCN), displace three solvents in a facial arrangement to chelate to a single metal center. Even with two such groups, the metal-metal bond is preserved by the presence of the acetates.⁴

Reactivity is not limited to the solvated side of the Mo-Mo unit. The acetate ligands may be selectively exchanged for a different carboxylate by stirring the initial compound in the incoming carboxylic acid for 12 h. The acetonitrile ligands remain on the molecule while ligand substitution occurs.⁵ It is interesting to note that the substituted species with menthoxyacetate and propenoate prepared by this method are effective room temperature catalysts for the polymerization of cyclopentadiene.⁵

Both the Mo and Rh systems offer a versatile combination of solvation and cationic charge. Reactions of these dications with dinuclear transition metal anions were investigated in the expectation that the resulting partially solvated mixed-metal salts could be used as precursors for mixed-metal clusters or extended solids. The isolation and characterization of several products isolated from these reactions are described herein.

B. Experimental, Synthesis

(1) Synthesis of $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ (1)

(i) Method 1

The starting materials, $[Rh_2(OAc)_2(MeCN)_6][BF_4]_2$ and $[n-Bu_4N]_2[Re_2Cl_8]$ were prepared by literature methods.^{1b,6} In a typical reaction, 116 mg of $[Rh_2(OAc)_2(MeCN)_6][BF_4]_2$ (0.156 mmol) and 175 mg of $[n-Bu_4N]_2[Re_2Cl_8]$ (0.153 mmol) were stirred in 15 mL of MeCN for 90 min. A lavender precipitate in a navy blue solution began forming within *ca*. five min. After 30 min, the solid was allowed to settle out, the solvent was decanted and the purple solid was washed with 4 x 10 mL of MeCN to remove residual $[n-Bu_4N][BF_4]$ and dried *in vacuo*; yield was 132 mg, (70%). IR (CsI, Nujol), cm⁻¹: 2329 (w), 2308 (w), 2304 (w), 2280 (w), 1555 (m), 1538 (m), 1057 (m), 1037 (m), 338 (s).

(ii) Method 2

A quantity of $[Rh_2(OAc)_2(MeCN)_6][BF_4]_2$ (116 mg, 0.156 mmol) was dissolved in 5 mL of MeCN to give a burgundy colored solution which was layered over a teal blue solution of $[n-Bu_4N]_2[Re_2Cl_8]$ (175 mg, 0.153 mmol) dissolved in a mixture of MeCN and CH_2Cl_2 . Ratios of this solvent mixture varied from 18:0.2, to 10:1 to 3:2 mL of MeCN : CH₂Cl₂. Air was accidentally leaked into the first reaction through an open stopcock, and subsequent experiments showed that this expedited crystal growth. Slow diffusion of the two reactant solution layers afforded a large amount of black microcrystalline needles that tended to grow from a single point in "bow tie" fashion from a dark navy solution. Chilling the Schlenk tube increased the amount of crystals formed, but generally they were not of X-ray quality. Crushing the dark crystals produced a lavender powder. Single crystals of this compound suitable for X-ray study were obtained from the first solvent ratio, but repeated attempts to reproduce larger crystals led to only microcrystalline product. After the solvent was removed by decanting, the crystals were washed with several 10 mL portions of MeCN and dried in vacuo. Yield 60 mg, (32%). Reducing the volume of the decanted solution led to further precipitation of the lavender product. IR data (CsI, Nujol), cm⁻¹: 2327 (m), 2311 (w), 2301 (w), 2279 (m), 1557 (s), 1538 (s), 1029 (m), 335 (s). Anal. Calcd for C₁₆H₂₄Cl₈N₆O₄Re₂Rh₂: C, 15.67; H, 1.97; Cl, 23.13. Found: C, 15.95; H, 2.05; Cl, 24.59.

(2) Reaction of [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈] in MeCN

A sample of 1 in the form of either the lavender solid or black microcrystals was suspended in a small volume of MeCN (2-5 mL). The salt was initially insoluble, but gradually dissolved to form an intensely blue colored solution with no sign of residual solid. For 20 mg of solid, (0.016 mmol) this process was complete within 24 h. The solution was subjected to a dynamic vacuum to produce a green residue which inevitably formed a glassy coating on the walls of the vessel. The solid dissolved in MeCN and MeOH to yield a blue solution and in acetone to yield a kelly green solution. The product was slightly soluble in CH_2Cl_2 in which it produces a pale green solution and was insoluble in diethyl ether, benzene, hexanes, and toluene. Crystallization attempts from MeCN/toluene appeared to yield two different solid products. Other solvent combinations did not yield precipitates. IR (CsI, Nujol), cm⁻¹: 2330 (w), 2300 (w), 1554 (m), 1520 (m), 1030 (w), 720 (m), 350 (s), 320 (m).

(3) Reaction of $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ in CH_2Cl_2

A small amount of the lavender solid 1 (20 mg, 0.016 mmol) was suspended in *ca*. 4 mL of CH₂Cl₂. After 2 h, the solid had become a slate blue color without dissolving and the solution was a pale green color. After standing for three weeks, the solution was yellow-brown, but the slate blue solid remained. The CH₂Cl₂ solution ($\lambda_{max} = 670$ nm) was decanted and reduced to a yellow residue which did not dissolve in MeCN. After MeCN was added to the blue solid, it reverted back to the original lavender color, again without dissolving.

(4) Reaction of [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈] in Acetone

A small volume of acetone (3-5 mL) was added to a sample of the lavender solid, 1 (20 mg, 0.016 mmol). Within 2 h, the solvent had turned turquoise green, but most of the lavender solid remained undissolved. After

32

standing for three weeks, the solution was emerald-green, but the suspended solid was a forest green color. IR of the forest green solid, (CsI, Nujol), cm⁻¹: 2330 (w), 2300 (w), 1680 (s), 1550 (s), 1238 (m), 1028 (w), 340 (vs). The solution was decanted from the solid and reduced to a residue (IR on the green residue from evaporation {CsI, Nujol}, cm⁻¹: 2330 (w), 2300 (w), 1690 (w), 1600 (w), 1520 (w), 690 (m), 345 (m), 320 (m)) which turned to teal green when redissolved in MeCN (λ_{max} : 610, 323 nm). The forest green solid became a dark yellow-green upon exposure to MeCN.

(5) Reaction of [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈] in THF

Addition of THF (ca. 2-5 mL) to a sample of the lavender product, 1, (20 mg, 0.016 mmol) produced a pale blue solution over a mixture of blue and purple solids within 2 h. Prolonged exposure for ~3 weeks led to a greenish-yellow solution and a blue solid. The solvent ($\lambda_{max} = 600$ nm) was decanted and reduced to a residue of a quantity insufficient for analysis. The blue solid (IR {CsI, Nujol}, cm⁻¹: 2325 (w), 2300 (w), 1565 (m), 1550 (m), 1030 (m), 880 (m), 338 (s)) was dried *in vacuo* and formed a pink/blue dichroic solution when exposed to MeCN. (UV-visible in MeCN, λ_{max} at 680 and 545 nm.)

(6) Thermal Reaction of [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈] in the Solid State

A quantity of 1, (40 mg, 0.033 mmol) was placed in a Schlenk tube and warmed gently in an oil bath. At 80°C, there was no apparent change. After heating at 95° for an hour, the solid turned olive green. Further temperature increase to 145° did not appear to effect any further reaction. The flask was cooled to room temperature, and was subsequently evacuated under dynamic vacuum to remove any liberated MeCN solvent. (IR on the olive green solid {CsI, Nujol}, cm⁻¹: 2335 (w), 2310 (w), 2284 (w), 1550 (s), 1030 (m), 340 (s)). Addition of 3 mL of MeCN to the solid gave a green solution and a brown solid. IR on the brown solid (CsI, Nujol), cm⁻¹: 1540 (m), 1020 (w), 690 (w), 350 (m,br).

(7) Work-up of Layer Reaction solutions

After the product was isolated from the $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ crystallization reactions in Synthesis Method 2, the decanted solutions were stored aerobically in vials. After several days, the MeCN/CH₂Cl₂ solutions had turned dichroic wine/blue and had produced a small amount of white precipitate. ($\lambda_{max} = 605$ nm, shoulder at 430 nm). The solid was removed by filtration, and several combinations of CH₂Cl₂, acetone, diethyl ether and MeCN were used in an attempt to isolate a pure compound without success.

(8) Reaction of [Rh₂(OAc)₂(MeCN)₆][BF₄]₂ with Chloride ion

An amount of $[Rh_2(OAc)_2(MeCN)_6][BF_4]_2$ (0.040 g, 0.054 mmol) and 0.0505 g of ppnCl (0.088 mmol) was stirred in 5 mL of MeCN at room temperature. Within two minutes, the solution had turned dark bluishpurple. After 24 hours, a fluffy green solid settled out of a pinkish-purple solution. (UV-visible of purple solution, $\lambda_{max} = 550$ nm). The solvent was decanted, and the solid was washed with 5 mL of MeCN. (IR data for the green solid {CsI, Nujol}, cm⁻¹: 2330 (w), 2300 (w), 1560 (s), 1020 (s), 370 (vw), 310 (vw).) The green solid was soluble in CH₂Cl₂ to give a UV-visible λ_{max} of 610 nm.

(9) Control reaction of [Re₂Cl₈]²⁻ with MeCN

A sample of $[n-Bu_4N]_2[Re_2Cl_8]$ was dissolved in MeCN and stored at room temperature for a week in order to note if any decomposition had occurred. The electronic spectrum verified the presence only of the original compound, ($\lambda_{max} = 680$ nm).

C. Experimental, Crystallography [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈]

(i) Data Collection and Reduction.

Due to difficulties with refinement of the original data set, a second crystal was also studied by X-ray methods and the results are given here. A black single crystal of 1 grown by Synthesis Method 2 and having approximate dimensions $0.7 \ge 0.2 \ge 0.2$ mm was mounted with epoxy on a glass fiber and was examined on a CAD-4 diffractometer at several temperatures. A preliminary cell was established by centering on reflections chosen from a rotational photograph and the final cell was indexed on 25 reflections with $21 \le 20 \le 28.3^{\circ}$. Axial photographs, as well as photographs of the [111] and [110] diagonals, verified the choice of orthorhombic symmetry rather than tetragonal in spite of two axes exhibiting nearly identical lengths. Five slightly different cells were obtained at various temperatures and are shown in Table 1. Although the cell parameters varied as the temperature was lowered, the symmetry did not reach tetragonal.

Intensity data were collected at -100 ± 2 °C over the range 4-45° using the ω -scan mode. Three periodically monitored standard reflections were collected every hour and indicated the crystal decayed by an average of 6.7%.

Table 1. Unit Cells of [Rh2(OAc)2(MeCN)6][Re2Cl8] determined atdifferent temperatures

Temp in °C	23	0	-8	-50	-100
a	27.23(1)	27.05(1)	27.52(4)	26.875(4)	27.42(1)
b	27.521(3)	27.504(7)	27.00(4)	27.482(9)	26.736(4)
с	18.203(2)	18.193(5)	18.22(5)	18.164(5)	18.137(5)
α	89.99(1)	89.92(2)	89.89(4)	90.03(2)	90.03(2)
β	89.98(2)	89.99(3)	89.92(5)	90.03(2)	90.04(3)
x	89.86(2)	90.03(3)	90.18(6)	89.98(2)	90.02(1)
volume	13643(6)	13535(9)	13540(20)	13415(6)	13296(7)

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9451 unique data were collected of which 5229 were observed with $F_0^2 \ge 3\sigma(F_0)^2$. Psi scans were applied to correct for absorption.

(ii) Structure Solution and Refinement.

All calculations were carried out on a VAXSTATION 4000 computer using the TEXSAN software package. The positions of the rhenium and rhodium atoms were established by application of the SHELXS-86 solution program.⁷ Most of the remaining non-hydrogen atoms were located using DIRDIF:⁸ alternating least squares and Fourier maps were used to locate and refine the rest of the atoms. A disorder of the Re4-Re5 metal unit became apparent quite early in the refinement. The occupancy of both orientations were experimentally determined and fixed for final refinement. Although Psi-scans had been applied to correct for absorption, the large number of heavy atoms in the structure led us to further correct for absorption by the use of the program, DIFABS. Unfortunately, this did not entirely alleviate the problem, as a large number of peaks in the final difference map were above 1.0 e⁻/Å³, 10 of which approached 2.0 e⁻/Å³. The highest peaks in the map were near the dirhenium units, but did not make chemical sense as disordered metal units. These peaks persisted even after anisotropic refinement of all metal and chloride atoms. The N and O atoms in the immediate coordination sphere of the two dirhodium units became nonpositive definite when refined anisotropically, so these and all the carbons were left isotropic. There were no non-positive definite atoms in the final refinement. The final full-matrix refinement involved 483 parameters and 5229 data for a data to parameter ratio of 10.8. The refinement converged with residuals of R = 0.078 and $R_w = 0.109$ and quality-of-fit = 2.64. The maximum shift/error in the last cycle was 0.05. The highest peak in the final

difference map was 2.88 e⁻/Å³ with about ten peaks of 2.0 e⁻/Å³ or below. A summary of the crystallographic data is found in Table 2.

D. Results and Discussion

Synthetic Methods

Our original intention in preparing mixed-metal salts was to pursue the possibility of stacking dinuclear transition metal units in the solid state in such a way that there would be conductivity along the M-M axes (See Figure 4). The Rh unit is most likely to form extended metal-metal interactions if the axial ligands could be removed.

The reaction to form 1 is a simple metathesis using very large constituent ions, shown in Figure 5. The insolubility of the mixed-metal salt not only in acetonitrile but all common solvents drives the reaction towards the kinetic product which is easily isolated before it has time to convert to the thermodynamic products. Since further reactivity upon prolonged exposure to solvents makes it impossible to recrystallize the sample, crystals may be grown only by slow diffusion of the reactants in solution. The slow rate of the diffusing solution produces crystals rather than a powder.

It might be expected that ions of this size would possess a rather low lattice energy, but this is apparently not the case. One consideration is that the ions are very well matched in size which is favorable for salt formation.

Spectroscopy

Infrared data verify that the lavender bulk product and the black microcrystalline product are the same compound. The IR spectrum is essentially an overlap of the corresponding spectra for the two starting

Formula	$Rh_2C_{16}N_6O_4Re_2CI_8$
Formula weight	1226.241
Space group	Pccn
a, Å	27.42(1)
b, A	26.736(4)
с, А	18.137(5)
α, deg	90
β, deg	90
γ, deg	90
V, Å ³	13296(7)
Z	16
d _{calc, g/cm³}	2.450
μ (Mo Kα), cm ⁻¹	90.05
Data collection instrument	CAD-4
Radiation (monochromated in incident beam)	Mo Kα(λα = 0.71073Å)
Temperature, °C	-100 ± 2
Scan method	ω
<i>Trans.</i> factors, max., min.	0.75 - 1.16
Ra	0.078
Rw ^b	0.109
$aR = \Sigma F_0 - F_c / \Sigma F_0 $	

Table 2. Crystal Data for [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈]

 $bR_{w} = [\Sigma w | F_{o} | - | F_{c} |)^{2} / \Sigma w | F_{o} |^{2}]^{1/2}; w = 1/\sigma^{2}(|F_{o}|)$

• •

Figure 4. Potential stacking configurations for the bridged and unbridged dimetal units

•



No Bridges



cis-Bridges



Figure 4

Figure 5. Diagram of the dinuclear ionic components of $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$

.


 $[\operatorname{Re}_2\operatorname{Cl}_8]^2$

Figure 5

materials. The v(Re-Cl) mode falls at about 335 cm⁻¹, and the prominent v(OCO) is centered at 1550 cm⁻¹. The v(C=N) stretching region between 2250 and 2350 cm⁻¹ is more complex than that of the [BF₄]⁻ precursor in this spectrum, presumably due to solid-state splitting effects. The starting material, $[Rh_2(OAc)_2(MeCN)_6][BF_4]_2$, exhibits three medium stretches of equal intensity in this region between 2340 and 2277 cm⁻¹. By comparison, the infrared spectrum of 1 displays a pattern wherein the two outer stretches are more intense than the inner stretches for a total of four bands in this region.

The electronic spectrum of the bulk $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ reaction solution is, again, a combination of the individual spectra for the starting materials, indicating a slight solubility of the salt in MeCN. The main features are at 680 nm { $\delta-\delta^*$ for $[Re_2Cl_8]^2$ } and 540 nm { $[Rh_2(OAc)_2(MeCN)_6]^{2+}$ }. Solid state resolution is not as great due to the sloping baseline, but electronic spectra on finely divided Nujol mull samples verified the existence of these two features in the solid salt as well.

Due to the general insolubility of the compound, accurate characterization was limited to the solid state. However, some information was obtained from freshly prepared solutions of the mixed-metal salt. Dissolution of the compound to produce a dilute sample in CD₃CN gave a ¹H NMR spectrum with primarily free CH₃CN at $\delta = 1.95$ ppm due to solvent exchange with the deuterated solvent. Very small singlet resonances were also observed at $\delta = 3.23$, 3.13, 2.12, 2.01, 1.99, and 1.97 ppm. None of these match particularly well with the spectrum of the [Rh₂(OAc)₂(MeCN)₆][BF₄]₂ which has singlets at $\delta = 2.54$ ppm due to equatorial MeCN, 2.04 ppm for bound acetate, and 1.95 ppm for the exchanged axial MeCN ligands. This result suggests that decomposition has taken place and there is, most likely, a mixture of products in the NMR sample.

Molecular Structure

Selected bond distances and angles for $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ are given in Table 3 and 4. Atomic positional parameters are included in the Appendix. An ORTEP packing diagram of the unit cell is shown in Figure 7 with a simplified representation in Figure 8. The asymmetric unit contains two unique dirhodium cations and one dirhenium anion on general positions, and two dirhenium units, one along a C_2 and the other bisected by a C_2 axis. Both of the dirhodium bis-acetate cation units gave similar bond distances and bond angles as the original structure with $[BF_4]$ as the counterion. ^{1c} The average Rh-Rh bond distance is 2.504(4)Å compared to 2.534(1)Å, the Rh-O is 2.01(3)Å compared to 2.015(4)Å, Rh-equatorial N of 1.97(3)Å compared to 1.983(4)Å, and Rh-axial N of 2.23(3)Å compared to 2.232(4)Å. One [Re₂Cl₈]²anion lies along a crystallographic C2 axis rendering the two Re atoms halfoccupied, each bound to two unique chlorides. Another [Re₂Cl₈]² is bisected perpendicular to the Re-Re bond, therefore only one Re atom and its attached four chlorides are unique. As far as we are aware, the present structure is the only one in which a $[Re_2X_8]^2$ unit is present in the same asymmetric unit with three different environments.9-11

A closer look at the packing diagram reveals the importance of cation shape on the local environments of the three unique $[\text{Re}_2\text{Cl}_8]^2$ units. One type of $[\text{Re}_2]^2$ unit can be seen to stack in an end-to-end fashion (Figure 8b) in a four-point star-shaped channel in which the chlorides point between the MeCN ligands of the $[\text{Rh}_2]^{2+}$ cations and toward the Rh atoms. The second independent $[\text{Re}_2\text{Cl}_8]^2$ unit forms a stack with perpendicularly aligned metal

Table 3. Selected Bond Distances in Å for [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈]

46

atom	atom	distance	atom	atom	distance
RE1	RE1'	2.225(4)	RE5	CL13	2.32(1)
RE1	CL1	2.31(1)	RE5	CL16	2.33(1)
RE1	CL2	2.28(1)	RH1	RH2	2.509(4)
RE1	CL3	2.33(1)	RH1	02	1.99(2)
RE1	CL4	2.32(1)	RH1	04	2.01(3)
RE2	RE3	2.216(3)	RH1	N4	1.98(3)
RE2	CL5	2.31(1)	RH1	N5	1.99(3)
RE2	CL5′	2.31(1)	RH1	N6	2.21(3)
RE2	CL6	2.32(1)	RH2	01	2.03(3)
RE2	CL6'	2.32(1)	RH2	03	1.99(2)
RE3	CL7	2.30(1)	RH2	N1	1.98(3)
RE3	CL7'	2.30(1)	RH2	N2	1.97(4)
RE3	CL8	2.32(1)	RH2	N3	2.23(3)
RE3	CL8'	2.32(1)			
RE4	RE5	2.215(4)			
RE4a	RE5a	2.20(1)			
RE4	CL11	2.31(1)			
RE4	CL12	2.32(1)			
RE4	CL14	2.29(1)			
RE4	CL15	2.30(1)			
RE5	CL9	2.35(1)			

2.31(1)

CL10

RE5

Table 3. continued

atom	atom	distance	atom	atom	distance
01	C1	1.40(4)	RH4	N7	1.90(3)
02	C1	1.29(4)	RH4	N8	1.99(3)
03	C3	1.24(4)	RH4	N9	2.22(3)
04	C3	1.37(5)	05	C17	1.31(5)
N1	C5	1.11(5)	06	C17	1.21(4)
N2	C7	1.14(5)	07	C19	1.26(4)
N3	C9	1.12(4)	08	C19	1.21(4)
N4	C11	1.12(4)	N7	C21	1.10(5)
N5	C13	1.11(4)	N8	C23	1.15(5)
N6	C15	1.10(4)	N9	C25	1.15(4)
C1	C2	1.42(6)	N10	C27	1.22(5)
C3	C4	1.34(5)	N11	C29	1.14(4)
C5	C6	1.51(5)	N12	C31	1.07(5)
C7	C8	1.50(7)	C17	C18	1.50(5)
C9	C10	1.55(5)	C19	C20	1.52(7)
C11	C12	1.57(6)	C21	C22	1.58(6)
C13	C14	1.45(5)	C23	C24	1.44(6)
C15	C16	1.53(6)	C25	C26	1.49(5)
RH3	RH4	2.498(4)	C27	C28	1.42(5)
RH3	06	2.03(2)	C29	C30	1.53(5)
RH3	07	2.01(2)	C31	C32	1.38(5)
RH3	N10	2.00(3)			
RH3	N11	1.96(3)			
RH3	N12	2.26(4)			
RH4	05	2.07(3)			

1.97(3)

RH4

80

atom	atom	atom	angle	atom	atom	atom	angle
RE1	RE 1	CL1	104.9(3)	CL7	RE 3	CL8	86.8(4)
RE1	RE1	CL2	103.2(3)	CL7	RE3	CL8	86.8(4)
RE 1	RE 1	CL3	104.6(3)	CL7	RE 3	CL8	87.0(4)
RE 1	RE 1	CL4	104.2(3)	CL8	RE3	CL8	152.3(5)
CL1	RE1	CL2	86.3(4)	RE5	RE4	CL11	101 8(4)
CL1	RE1	CL3	150.4(4)	RE5	RE4	CL12	102.7(4)
CL1	RE1	CL4	86.4(4)	RE5	RE4	CL14	102.7(4)
CL2	RE1	CL3	87.1(4)	RE5	RE4	CL15	104.1(3)
CL2	RE1	CL4	152.7(5)	CL11	RE4	CL12	85 5/5
CL3	RE1	CL4	86.4(5)	CL11	RE4	CL14	88 7(5)
RE 3	RE2	CL5	103.9(2)	CL11	RE4	CL15	154 1/51
RE 3	RE2	CL5	103.9(2)	CL12	RE4	CL14	154 4(5)
RE3	RE2	CL6	104.0(2)	CL12	RE4	CL15	87 5(4)
RE3	RE2	CL6	104.1(2)	CL14	RE4	CL15	87 0(4)
CL5	RE2	CL5	152.2(5)	RE5A	RE4A	CT.15	107 0/2
CL5	RE2	CL6	86.3(4)	CL9	RE4A	CL10	107.0(2) 87.2(E)
CL5	RE2	CL6	87.0(4)	CL9	RE4A	CL14	87 4 (5)
CL5	RE2	CL6	87.0(4)	CL9	RE4A	CL15	152 (16)
CL5	RE2	CL6	86.3(4)	CL10	RE4A	CL14	153 9(6)
CL6	RE2	CL6	151.9(4)	CL10	RE4A	CL15	88 0/5
RE2	RE 3	CL7	102.9(2)	CL14	RE4A	CL15	84 9(5)
RE2	RE 3	CL7	103.0(2)	RE4	RE5	CL9	101 5/3
RE2	RE 3	CL8	103.8(2)	RE4	RE5	CL10	103.0(3)
RE2	RE 3	CL8	103.9(2)	RE4	RE5	CL13	105.0(3)
CL7	RE3	CL7	154.0(5) ·	RE4	RE5	CL16	
CL7	RE3	CL8	87.0(4)				(4)

Table 4. Selected Bond Angles in degrees for [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈]

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

atom	atom	atom	angle	atom	atom	atom	angle
CL9	RE5	CL10	87.1(4)	02	RH1	N6	89(1)
CL9	RE5	CL13	87.4(4)	04	RH1	N4	91(1)
CL9	RE5	CL16	154.2(5)	04	RH1	N5	178(1)
CL1 0	RE5	CL13	151.5(5)	04	RH1	N6	94(1)
CL10	RE5	CL16	87.5(4)	N4	RH1	N5	91(1)
CL13	RE5	CL16	85.3(4)	N4	RH1	N6	90(1)
RB4A	RE5A	CL11	96.1(6)	N5	RH1	N6	86(1)
RE4A	RE5A	CL12	96.5(6)	RH1	RH2	01	87.0(6)
RE4A	RE5A	CL13	106.0(6)	RH1	RH2	03	84.9(6)
RB4A	RE5A	CL16	109.0(6)	RH1	RH2	Nl	95.2(9)
CL11	RE5A	CL12	78.0(5)	RH1	RH2	N2	98.3(9)
CL11	RE5A	CL13	89.5(6)	RH1	RH2	N3	174.0(8)
CL11	RE5A	CL16	153.3(7)	01	RH2	03	88.0(9)
CL12	RE5A	CL13	155.3(7)	01	RH2	N1	178(1)
CL12	RE5A	CL16	89.6(6)	01	RH2	N2	87(1)
CL13	RE5A	CL16	92.5(7)	01	RH2	N3	89(1)
RH2	RH1	02	86.1(6)	03	RH2	N1	93(1)
RH2	RH1	04	83.4(9)	03	RH2	N2	174(1)
RH2	RH1	N4	95.0(8)	03	RH2	N3	90(1)
RH2	RH1	N5	97.1(7)	Nl	RH2	N2	92(1)
RH2	RH1	N6	174.0(9)	Nl	RH2	N3	89(1)
02	RH1	04	88(1)	N2	RH2	N3	86(1)
02	RH1	N4	179(1)				
02	RH1	N5	90(1)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

atom	atom	angle	atom	atom	atom	angle
RH3	06	83.6(6)	06	RH3	N12	92(1)
RH3	07	84.6(6)	07	RH3	N10	95(1)
RH3	N10	98.0(9)	07	RH3	N11	177(1)
RH3	N11	96.4(7)	07	RH3	N12	91(1)
RH3	N12	173.6(9)	N10	RH3	N11	87(1)
RH3	07	85.0(9)	N10	RH3	N12	87(1)
RH3	N10	178(1)	N11	RH3	N12	88(1)
RH3	N11	93(1)	RH3	RH4	05	86.2(7)
			RH3	RH4	08	83.3(8)
			RH3	RH4	N7	99.3(9)
			RH3	RH4	N8	95.5(9)
			RH3	RH4	N9	172.8(8)
			05	RH4	08	89(1)
			05	RH4	N7	174(1)
			05	RH4	N8	92(1)
			05	RH4	N9	87(1)
			08	RH4	N7	88(1)
			08	RH4	N8	178(1 <u>)</u>
			08	RH4	N9	95(1)
			N7	RH4	N8	90(1)
			N7	RH4	N9	87(1)
			N8	RH4	N9	87(1)

Table 4. continued

atom RH4

RH4

RH4 RH4

RH4

06 06

06

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Figure 6. ORTEP unit cell packing diagram for

 $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$



Figure 6

Figure 7. Schematic diagram of the unit cell of [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈] showing the packing orientation of the Re-Re units. The singly labeled locations are units parallel to the viewing angle. The Rh-Rh units are located in the empty boxes.



Figure 7

Figure 8. Representation of the three stacking modes of Re-Re units in the crystal, $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$



units (Figure 8c) in a second smaller star-shaped channel. Finally, the third unique rhenium atom (8a) displays a parallel stacking of M-M units in a larger, ill-defined channel bordered by acetate groups of the surrounding dirhodium cations. This unit is the only type of octachlorodirhenate in the structure to exhibit disorder of the metal unit, a feature found for the $[\text{Re}_2\text{Cl}_8]^2$ groups in all of the salts in which it has been crystallized. The minor orientation has an occupancy of 19% which is within the range reported for other examples.⁹

A comparison of the Re-Re separations in the three different types of $[\text{Re}_2\text{Cl}_8]^2$ ions are of interest in this study. The three values of 2.225(4) for Re1-Re1, 2.216(3) for Re2-Re3, and 2.215(4) for Re4-Re5 are at the lowest end of the range of values for Re-Re bond which vary from 2.46(8)Å for [2,4,6-(CH_3)_3C_5H_2NH]_2Re_2Cl_8 to 2.21(1)Å for [(DMF)_2H]_2Re_2Cl_8.^{12} Of the two units in the current structure that are shorter than any of the known values, Re2-Re3 possesses no disorder, and Re4-Re5 possesses the aforementioned disorder of 81% / 19% (vice supra).

Study of structures containing the $[M_2L_8]^2$ core with various ligands has recently been the focus of attention by Cotton and coworkers. It is their goal to establish the influence of counterion and ligand on the crystal packing forces of the molecule. In no cases previous to our work has a dication of this large size been used. It has been established from many independent X-ray results that the M-M unit in M₂L₈ systems tends to pack in a disordered manner; the magnitude of which depends on the counterion and the supporting ligands. At one extreme is $[n-Bu_4N]_2[Re_2I_8]$ where the salt is quite loosely packed and the metal-metal unit disorders equally over all three possible orientations.⁹ The other extreme is represented by $[n-Bu_4N]_2[Re_2F_8]$ for which no disorder was observed.¹⁰ These two disparate results underscore the influence of the ligands; the large, highly polarizable iodides provide no discrimination for the M-M orientation while the small, hard fluorides distinctly prefer only one site for the dimetal unit. More commonly, crystal structures of $[M_2X_8]^{2}$ complexes where X = Br, or Cl tend to have one major orientation with one minor orientation being occupied between 5 and 40 %.¹¹ This maximum value was obtained for the crystal structure of [n- $Bu_4N]_2[Re_2Br_8]$.^{11c}

Reactions of [Rh₂(OAc)₂(MeCN)₆][Re₂Cl₈]

Monitoring the electronic spectrum of the reaction solution of $[Rh_2(OAc)_2(MeCN)_6][BF_4]_2$ and $[n-Bu_4N]_2[Re_2Cl_8]$ showed that over time, the characteristic features of these two compounds disappeared and a broad new feature grew in at 610 nm, shown in Figure 9. This feature similarly appeared when the lavender solid of 1 was dissolved over time in MeCN. The infrared spectra of the kinetic and redissolved products also differed, further supporting the formation of a new thermodynamic product upon dissolution of the kinetic product 1. The original complicated pattern in the v(C=N)region of the $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ solid state infrared spectrum collapsed into two bands, and the v(Re-Cl) stretch in the far-IR region broadened and changed from one stretch at 338 cm^{-1} to one at 350 with ashoulder at 320 cm⁻¹. A ¹H NMR spectrum of the residue displays, once again, principally free MeCN at $\delta = 1.95$ ppm, but also exhibits singlet resonances at 3.26, 3.13, and 2.54 ppm. It is assumed that the 2.54 feature is due to equatorial MeCN. There are a number of other features reminiscent of the earlier NMR spectrum ($\delta = 2.48, 2.37, 2.14, 2.01, 1.99$, and 1.98 ppm), but these are of much lower intensity than the others. We concluded from this

Figure 9. Qualitative Electronic Spectra of the Kinetic and Thermodynamic Products of the Reaction between [Rh₂(OAc)₂(MeCN)₆][BF₄]₂ and [n-Bu₄N]₂[Re₂Cl₈]. (1) Solution from initial reaction in MeCN. (2) Kinetic salt in MeCN for 24 h. (3) Thermodynamic product(s) in MeCN.



Wavelength (in nm)

result that the chemistry is complicated, and is quite likely producing a mixture of several species.

Numerous efforts to elucidate the identity of the new compound met with limited success. If ligand redistribution were occurring, it would seem that either $[Re_2Cl_8]^{2-}$ was not stable in MeCN, or the $[Rh_2]^{2+}$ unit was abstracting chloride from the $[Re_2]^2$ anion. To test the first hypothesis, a sample of $[n-Bu_4N]_2[Re_2Cl_8]$ was dissolved in MeCN and stirred for a week after which time the electronic spectrum was measured which showed no sign of decomposition ($\lambda_{max} = 680$ nm). The second hypothesis was tested by reacting two equivalents of a soluble Cl^- source, namely ppnCl, to the $[Rh_2]^{2+}$ unit. This chemistry did not proceed cleanly, nevertheless we noted that the product's properties did not match those of the thermodynamic product. An IR spectrum of the lime-green compound displayed two weak stretches in the v(C=N) region, but did not show substantial v(Rh-Cl) features. The electronic spectrum of this solid in MeCN exhibited one absorption at 550 nm, which is not the same as that seen for the thermodynamic product. Subsequent experiments in our labs revealed that the reaction of $[Rh_2(OAc)_2(MeCN)_6]^{2+}$ with ppnCl yields three different products including $Rh_2(OAc)_2(MeCN)_4Cl_2$, Rh₂(OAc)₄(MeCN)₂, and [ppn][RhCl₄(MeCN)₂] which are purple, green, and orange respectively.¹³ None of these compounds resembles the blue thermodynamic product of the mixed-metal reaction.

The difference between the experiments involving redissolution of the purified product in fresh solvent and working up the layer reaction solutions lies in the presence of $[n-Bu_4N][BF_4]$ in the solution. If the kinetic salt is isolated before further reaction occurs, only the dimetal units, their ligands, and the solvent may take part in further reaction. The layer reaction solutions contain the soluble by-product, $[n-Bu_4N][BF_4]$ which may also

61

participate in further chemistry. The presence of $[n-Bu_4N][BF_4]$ may alter the subsequent reaction pathway due to the enhanced electrolyte concentration or it may participate in the transformation of the $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ salt.

The most likely site of reactivity in the mixed-metal ion salt 1 is at the labile axial position of the dirhodium cation. Such a reaction would be accompanied by color changes with different donor types, which indeed was observed with the various dissolution attempts of 1. We decided to further explore the reactivity of 1 without solvent which would encourage condensation reactions of the two metal units. The lavender solid was heated to 145 °C in the solid state. An olive compound was produced, and washing with MeCN gave a green solution and an insoluble brown solid. Successful removal of coordinated solvent ligands was confirmed by infrared spectroscopy, as the olive solid displays very weak v(C=N) stretches and the brown compound does not give any evidence for MeCN in the 2200-2300 cm⁻¹ region. The loss of the MeCN ligands in the solid-state reaction required forcing conditions. Such a product is not forming in the solution decomposition reactions of 1, as the resulting solids from these experiments reveal several medium intensity features in the acetonitrile region. Thus it is reasonable to assume that solvent plays an important role in the chemistry upon redissolution of 1 and that this reaction pathway is inaccessible without this medium. In light of these experiments, the reactivity of the kinetic product 1 with other solvents is more easily explained. The solvent, CH_2Cl_2 , with little coordinating ability, does not substantially alter the identity of the original salt as verified by the solid reverting to lavender upon exposure to MeCN. Only a very small amount of the solid is dissolved. For THF, acetone, and MeCN, the coordinating ability is more significant so more of the salt

dissolves (all in the case of MeCN) and the lavender solid can not be regenerated by addition of MeCN. All three solids display IR activity in the v(C=N) region around 2300 cm⁻¹ indicating that some, but not total solvent exchange has occurred. It is apparent that the ability of the solvent to act as a ligand contributes to the further reactivity of the salt.

E. Summary and Future Directions

The unusual soft salt $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ was isolated by taking advantage of the insolubility of this compound in common solvents. Although this product was fully characterized, the product or mixture of products formed by its decomposition in MeCN were not identified. Straightforward ligand redistribution does not seem to be responsible for the new products. Of the solvents studied other than MeCN, redissolution of 1 in acetone gives the best solubility; perhaps the products of this reaction may be isolated more easily and then compared to the inconclusive MeCN data.

Preparation of the Mo analog with $[\text{Re}_2\text{Cl}_8]^2$ would be an extremely valuable comparison. Several researchers in our group have verified that there is no initial precipitation of product in this reaction as is seen in the aforementioned work. Most of these experiments have been accidentally exposed to air after about an hour, so repeating these reactions under rigorously anaerobic conditions should lend more insight into the general nature of this system.

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CHAPTER III

SYNTHESIS AND REACTIVITY OF

SOLVATED DIRHODIUM CATIONS

A. Introduction

Metal complexes ligated solely by neutral solvent groups have the advantage of lacking strong donors that direct the location and number of incoming groups through electronic trans effects.¹ The relatively small size of common weak donor solvents that act as ligands such as water, nitriles, alcohols, and THF, also reduces the cis-steric effects near the reaction site. Since they lack anionic or bulky ligands such as halides, phosphines, and carboxylates, fully solvated complexes may be used as synthons in the systematic design of new molecules based on number of equivalents and the relative trans effects of the new ligands rather than on the stoichiometry and disposition of substituents on the starting material.

The importance of $[Rh_2(MeCN)_{10}]^{4+}$ as an excellent unhindered starting material was first verified in its reaction with the highly bulky and basic functionalized phosphine, TMPP (TMPP = tris(2,4,6trimethoxyphenyl)phosphine).² The Rh₂ unit undergoes non-redox homolytic bond cleavage to yield a rare example of a stable mononuclear Rh(II) d⁷ radical, $[Rh(TMPP)_2][BF_4]_2$. In comparison, reaction of the same phosphine with the tetra-bridged rhodium acetate, a more common starting material for this metal, leads to the removal of only one bridging group while the Rh₂ unit remains intact.³ Clearly, the absence of bridging ligands in the $[Rh_2(MeCN)_{10}]^{4+}$ complex promises to enable access to many new compounds.

A comprehensive investigation of synthetic routes into the $[Rh_2L_{10}]^{4+}$ core, in addition to study of the elementary reactivity trends, is vital to the full realization of the potential of this system as a synthon, and will also assist our further efforts to design and prepare new compounds.

66

B. Experimental, Synthesis

(1) Preparation of Rh₂(OAc)₄(MeCN)₂

RhCl₃ was obtained from either Sigma or through a precious metal loan from Johnson-Matthey. In the course of experimentation, it was found that the commonly used $Rh_2(OAc)_4(MeOH)_2$ was often contaminated with excess sodium acetate not removed during the MeOH recrystallization step in the synthesis.⁴ Thus later reactions with this starting material utilized a different axial adduct, $Rh_2(OAc)_4(MeCN)_2$, which was formed by an extra recrystallization of the tetraacetate from MeCN. The free acetate impurity is far less soluble in MeCN than in MeOH, therefore more effective separation is achieved. The crude dirhodium product can not be directly converted to the MeCN adduct as the HOAc axial adduct is insoluble in MeCN.

(2) Preparation of $[Rh_2(MeCN)_{10}][BF_4]_4$ (2)

(i) Method 1

Rhodium tetraacetate was prepared by literature methods.⁴ In a typical reaction, $Rh_2(OAc)_4(MeOH)_2$ (200 mg, 0.395 mmol) was refluxed in a mixture of 5 mL of a 1 <u>M</u> solution of Et₃OBF₄ in CH₂Cl₂ (excess) and 10 mL of MeCN under N₂ at atmospheric pressure. Large orange crystals began to form in the red-orange solution after several days. After seven days of reflux, the crop of crystals was removed by filtration under an inert atmosphere, washed with two 5 mL amounts of CH₂Cl₂ followed by diethyl ether, and dried *in vacuo*. The volume of the filtrate was reduced to a low volume (~ 1 mL) and chilled to -20°C. Additional product was precipitated from the concentrated filtrate by addition of CH₂Cl₂ (about 4 mL). The remaining pale orange solution was decanted from the mixture of crystalline and solid product. The orange [Rh₂(MeCN)₁₀][BF₄]₄ salt was recrystallized from pure acetonitrile by alternating cycles of reducing the volume and chilling; yield, 260 mg (70%). The solid complex is hygroscopic as evidenced by its facile reaction with moist air to form the pink axial bis-water adduct. The salt is soluble in MeCN, H₂O, DMSO, and CH₃NO₂, but is insoluble in THF, alcohols, acetone, and CH₂Cl₂. Anal. Calcd for C₂₀H₃₃B₄F₁₆N₁₀Rh₂: C, 24.93; H, 3.13; F, 31.55. Found: C, 25.44; H, 3.58; F, 31.37. IR (CsI, Nujol), cm⁻¹: 2342 (m), 2317 (m), 2300 (w), 1062 (vs, br), 1024 (vs, br). ¹H NMR (CD₃CN, anaerobic): $\delta = 1.95$ ppm (singlet). UV-visible (MeCN, anaerobic): λ_{max} , nm (ϵ in <u>M</u>⁻¹cm⁻¹) = 468 (570), 277 (24,400).

(ii) Method 2

In a typical reaction, a mixture of $Rh_2(OAc)_4(MeOH)_2$ (200 mg, 0.395) mmol), 10 mL of MeCN, and 1 mL of HBF_4 /diethyl ether complex in diethyl ether (excess) were refluxed for ten days. After ca. seven days, an additional quantity of $HBF_4 \cdot Et_2O$ complex (0.7 mL) was added to ensure complete reaction. The initial solution was a dark purple and gradually changed to a reddish orange color. (If the solution remains red, more $HBF_4 \cdot Et_2O$ should be added.) The reaction solution was allowed to cool, after which hexanes. and diethyl ether were layered on top to precipitate the product. Hexanes and MeCN are immiscible so placing a layer of hexanes between the MeCN and diethyl ether insures a good interface. The diethyl ether diffuses into the hexanes, and the resulting mixture is miscible with MeCN so complete diffusion occurs with the production of large rod-shaped crystals. The original reaction solutions often contain brown or black impurities, so the solid must be recrystallized by the acetonitrile/hexanes/diethyl ether method. Yields averaged between 60 and 70% (228 to 266 mg). The product was characterized as in Method 1.

(3) Metathesis of [Rh₂(MeCN)₁₀][BF₄]₄ with LiTFMS

A quantity of 2 (164 mg, 0.170 mmol) and a ten-fold excess of lithium trifluoromethanesulfonate, (1.125 g, 7.20 mmol, 42.4 equiv.) were dissolved in 20 mL of MeCN. The solution was warmed gently to dissolve the last of the rhodium starting material. Alternating volume reduction and chilling yielded a crop of bright orange microcrystals which were washed with diethyl ether after the supernatant solution was removed by decantation. IR data indicated that only a small amount of [BF₄]⁻ remained, but the product yield was greater than theoretical, implying that the product was contaminated by excess LiTFMS (yield = 225 mg, theoretical yield = 206 mg). Subsequent recrystallizations did not appear to effectively purify the product which was visibly admixed with a white contaminant. IR (KBr, Nujol), cm⁻¹: 2345 (s), 2319 (m), 2293 (m), 1306 (vs), 1252 (vs), 1235 (vs), 1178 (vs), 1055 (vs), 643 (vs), 517 (s). ¹H NMR (d⁶-acetone, 5 min. after sample preparation) δ = 2.91 ppm (s).

(4) Metathesis of $[Rh_2(MeCN)_{10}][BF_4]_4$ with Sodium tosylate

Compound 2, (282 mg, 0.293 mmol) and sodium *p*-toluenesulfonate (1.117g, 5.75 mmol, 19.6 equiv.) were warmed gently in 20 mL of MeCN for 24 h. At this point there remained a large quantity of undissolved white solid, but the solution color had darkened with dissolution of the orange Rh salt. The solution was filtered by cannula, and the volume of the solution was reduced. The white solid was washed with 5 mL of MeCN which was combined with the solutions. The volume of the combined solutions was reduced again causing more white solid to precipitate. This was removed by filtration, and the volume of the resulting solution was reduced by one-half

69

and chilled to -20°C which led to the precipitation of an orange solid. Diethyl ether (3 mL) was added to encourage complete precipitation. IR data indicated no metathesis had occurred as evidenced by the presence of [BF₄]⁻ and the absence of [TFMS]⁻. IR (KBr, Nujol), cm⁻¹: 2344 (s), 2316 (m), 2281 (m), 1069 (vs, br).

(5) Metathesis of $[Rh_2(MeCN)_{10}][BF_4]_4$ with TBA(Tosyl)

A sample of 2 (211 mg, 0.219 mmol) and 362 mg of tetrabutylammonium *p*-toluenesulfonate (0.875 mmol, 4.0 equiv.) was dissolved in 20 mL of freshly distilled MeCN. Upon stirring in room light, the solution turned a red-brown color with a dark precipitate at the bottom. The reaction was then covered with foil and left to stir overnight. The next morning, the orange solution had yielded a large quantity of brown precipitate which was removed and discarded. Precipitation of the product from the filtrate was induced by reduction of the volume and addition of ether. The resulting orange solid was isolated by decanting off the supernatant and washing with several amounts (5 mL each) of diethyl ether. The product was dried *in vacuo*. The IR was the same as for the LiTFMS metathesis demonstrating that the $[BF_4]^-$ salt prevailed.

(6) Preparation of $[Rh_2(MeCN)_{10}][TFMS]_4$ (3)

An amount of $Rh_2(OAc)_4(MeCN)_2$ (200 mg, 0.382 mmol) was refluxed together with 0.5 mL of $Me_3SiTFMS$ (excess) and 10 mL of MeCN for two weeks. After ~ 1 week, an additional amount of $Me_3SiTFMS$ (0.5 mL) was added to aid in complete reaction. The red-orange solution was layered with hexanes and diethyl ether which produced large amounts of the crystalline product. The solution was decanted and the crystals were washed with copious amounts of CH₂Cl₂ and diethyl ether (2 x 5 mL each). The solid was dried by passing N₂ gas over the solid. Application of a dynamic vacuum to the solid for long periods of time led to a loss of crystallinity and conversion of the orange product to a purple solid. <u>Orange product:</u> IR (CsI, Nujol), cm⁻¹: 2345 (s), 2316 (s), 2286 (m), 1263 (vs), 1227 (vs), 1157 (s), 1030 (s), 756 (m), 640 (vs), 572 (m), 518 (vs). ¹H NMR (CD₃NO₂): $\delta = 2.79$ (s, 6H, equatorial CH₃CN), 2.02 (s, 1H, free CH₃CN). Integration is imprecise due to the breadth of the second resonance. <u>Purple product:</u> IR (CsI, Nujol), cm⁻¹: 2341 (m), 2316 (w), 1309 (m, split), 1267(s), 1228 (s), 1205 (s), 1157 (m), 1032 (s), 1018 (m), 1008 (s), 640 (s), 572 (w), 518 (m). ¹H NMR (CD₃NO₂): $\delta = 2.79$ (s, equatorial CH₃CN).

(7) Reaction of [Rh₂(MeCN)₁₀][TFMS]₄ with Methanol

Dissolution of 3 (30 mg, 0.025 mmol) in MeOH yielded a cherry red solution which turned green within hours with concomitant precipitation of black Rh metal. The solvent was removed by vacuum to produce a residue which dissolves in MeCN to form an orange solution and a black insoluble precipitate. The residue was completely soluble in THF to give a red-brown solution, while acetone, like MeCN, does not dissolve the black component. No spectral data were collected from this sample due to the very small residues remaining.

In separate experiments, an anaerobic UV-visible sample of 3 was aged in MeOH in room light for two hours. The initial spectrum ($\lambda_{max} = 514$ nm, shoulder at 381 nm) totally disappeared after two hours giving a featureless spectrum with no absorption maxima distinguishable from the tail into the ultraviolet region. An anaerobic solution IR in MeOH after 10 min. displayed three weak features (CaF₂ cells) cm⁻¹: 2359 (w), 2336 (m), and 2313 (w). These features faded into the baseline after the solution sat overnight in ambient light.

(8) Reaction of $Rh_2(OAc)_4(MeOH)_2$ with HTFMS and Acetonitrile

 $Rh_2(OAc)_4(MeOH)_2$, (111 mg, 0.219 mmol) was reacted with 0.5 of mL HTFMS (excess) in 5 of mL MeCN under reflux conditions for 18 h. The orange solution was cooled then filtered to remove a small amount of brown solid. The solution volume was reduced by one-half and 4 mL of CH_2Cl_2 were added to induce precipitation. The solution separated into two phases; the CH_2Cl_2 was removed by vacuum until the two phases mixed. Chilling the solution to -40 °C did not precipitate any solid, but instead produced an oil. Subsequent efforts to extract a solid from this solution were not successful.

(9) Reaction of Rh₂(OAc)₄(MeOH)₂ with MeTFMS

A sample of $Rh_2(OAc)_4(MeOH)_2$ (72 mg, 0.142 mmol) was reacted with 5 mL of freshly distilled MeCN and 0.3 mL of MeTFMS (excess). After six days of refluxing, an additional 1.5 mL of MeTFMS was added. The reaction was heated for ten days at which time the solution was opaque and oily redorange. Efforts to isolate a product by addition of diethyl ether, CH_2Cl_2 , or toluene to the oil and chilling to -40 °C did not prove helpful as all solvents tended to form immiscible layers with the reaction solution.

(10) Reaction of [Rh₂(MeCN)₁₀][BF₄]₄ with Propionitrile

A quantity of 2 (54.2 mg, 0.056 mmol) was stirred and warmed gently in 10 mL of EtCN for 12 h at which time the solution volume was reduced slightly and 15 mL of diethyl ether were added. Chilling to -40 °C precipitated a tan-orange solid. The solution was decanted, and the crystals

72

were dried *in vacuo*. IR (KBr, Nujol), cm⁻¹: 2345 (w), 2314 (w), 2288 (w), 1030 (m). ¹H NMR (CD₃CN,), ppm: $\delta = 2.35$, (q, 2 H, CH₃CH₂CN), 1.19 (t, 3 H, CH₃CH₂CN), 1.95 (s, unintegrated, free CH₃CN) indicating incomplete ligand exchange.

(11) Synthesis of [Rh₂(EtCN)₁₀][BF₄]₄ (4)

Rh₂(OAc)₄(MeCN)₂ (205 mg, 0.391 mmol), 10 mL of EtCN, and excess $(1 \text{ mL}) \text{ HBF}_4/\text{diethyl}$ ether complex were refluxed together for two days. The solution changed from purple to a bright red-orange. The solution was allowed to cool, whereupon hexanes and diethyl ether were carefully layered on top and allowed to diffuse slowly. A mixture of large crystals and orange oil resulted. The solution and the oil were decanted, and the crystals were washed with three 5 mL portions of 1:1 ether : propionitrile to remove the sticky residue. The washings were added to the decanted solution and the entire amount was reduced to a low volume, after which EtCN added to dissolve the oil, and finally hexanes and diethyl ether (1 mL and 10 mL respectively) were added to precipitate more product. This procedure was repeated until there was a negligible amount of oil. Combined yield of all. crystals, 290 mg, 67%. Anal. Calcd for $C_{30}H_{50}B_4F_{16}N_{10}Rh_2$: H, 4.57; C, 32.60; N 12.69. Found: H, 4.56; C, 31.08; N, 12.07. IR (CsI, Nujol), cm⁻¹: 2324 (s), 2287 (m), 1315 (w), 1285 (w), 1055 (vs, br), 783 (m), 561 (w), 521 (m). ¹H NMR (CD₃CN, anaerobic): $\delta = 3.03$ ppm (q, 8H, equatorial-CH₃CH₂CN), 2.35 (q, 2H, free CH_3CH_2CN), 1.36 (t, 12H, equatorial- CH_3CH_2CN), 1.19 (t, 3H, free $\underline{CH_3}CH_2CN$).

73

(12) Reaction of Rh₂(OAc)₄(MeOH)₂ with HTFMS and Propionitrile

An amount of $Rh_2(OAc)_4(MeOH)_2$ was combined with excess HTFMS (2 mL) and 5 mL of EtCN and refluxed for 24 h to yield an orange solution. Unfortunately, all attempts to isolate a solid by addition of either CH_2Cl_2 or diethyl ether/hexanes led only to oils or no precipitation at all.

(13) Reaction of Rh₂(OAc)₄(MeCN)₂ with Me₃SiTFMS and Propionitrile

A sample of $Rh_2(OAc)_4(MeCN)_2$ (100 mg, 0.191 mmol) was refluxed with an excess of $Me_3SiTFMS$ (l mL) in 5 mL of propionitrile for two weeks. After 7 days, an additional 0.5 mL of $Me_3SiTFMS$ was added to the solution. The resulting red-brown solution was cooled, layered with hexanes and diethyl ether (1 mL and 10 mL respectively), and chilled to -20 °C. A brown oil formed which did not resemble the color of the $[BF_4]^-$ salt; no solid product was obtained.

(14) Reaction of Rh₂(OAc)₄(MeCN)₂ with HBF₄ and Butyronitrile

An amount of $Rh_2(OAc)_4(MeCN)_2$ (102.5 mg, 0.196 mmol) was reacted with an excess of HBF₄ (1 mL) in 6 mL of deoxygenated PrCN under refluxing conditions. After 2 h, the solution was orange, nevertheless the reaction was heated overnight (~ 12 h) to ensure complete reaction. Addition of hexanes and diethyl ether (1 mL and ~ 10 mL) and subsequent chilling of the solution did not precipitate any solid.

(15) Reaction of $Rh_2(OAc)_4(MeCN)_2$ with Et_3OBF_4 and Butyronitrile

A quantity of $Rh_2(OAc)_4(MeCN)_2$ (102 mg, 0.196 mmol) was combined with 8 mL of PrCN and 4 mL of Et_3OBF_4 solution in CH_2Cl_2 (1 <u>M</u>) and refluxed for one day. The solution was allowed to cool at r. t., after which hexanes (1 mL) and diethyl ether (~ 10 mL) were added to initiate precipitation. An orange oil resulted, but no solid was isolated.

(16) Reaction of [Rh₂(EtCN)₁₀][BF₄]₄ with Butyronitrile

An amount of 4 (106 mg, 0.096 mmol) was stirred in 5 mL of PrCN at r. t. overnight. The compound readily dissolved to give an orange solution. Hexanes (1 mL) and diethyl ether (~ 10 mL) were layered on the solution after 1 day, but these efforts did not yield a tractable product.

(17) Reaction of [Rh₂(MeCN)₁₀][BF₄]₄ with Benzonitrile

A sample of 2 (50 mg, 0.052 mmol) was stirred in 5 mL of PhCN for 12 h. The solution (UV-visible shoulder at 450 nm) was filtered in air to yield 47.1 mg of a gold-yellow product which was dried by washing with diethyl ether. The ¹H NMR spectrum revealed an absence of benzonitrile (CD₃CN): $\delta = +1.95$ ppm (free CH₃CN). IR (CsI, Nujol), cm⁻¹: 2343 (s), 2314 (m), 2270 (w), 2243 (w), 1672 (m), 1603 (m), 1060 (vs, br). Redissolving the solid in benzonitrile and heating for 4 h led to the formation of an orange-brown solution. Addition of diethyl ether and chilling to 0 °C precipitated a pale tan solid which was washed with diethyl ether and dried *in vacuo*. The ¹H NMR spectrum of the product displayed no free MeCN (CD₃CN), ppm: $\delta = 7.74$ (m), 7.72 (d), 7.67 (t), 7.65 (t), 7.56 (m), 7.54 (m), 7.51 (m), and the IR spectrum showed all v(C=N) bands shifted from those of the starting material (CsI, Nujol), cm⁻¹: 2241 (m), 2226 (w), 1070 (s, br). Efforts to recrystallize the solid were not successful.

(18) Reaction of [Rh₂(EtCN)₁₀][BF₄]₄ with Benzonitrile

A quantity of 4 (120 mg, 0.109 mmol) was dissolved in 15 mL of warm deoxygenated PhCN to produce a dark orange-red solution. Addition of hexanes (1 mL) and diethyl ether (10 mL) did not lead to precipitation.

(19) Reaction of Rh₂(OAc)₄(MeCN)₂ with Pentanedinitrile

An amount of $Rh_2(OAc)_4(MeCN)_2$ (200 mg, 0.381 mmol), $NC(CH_2)_3CN$ (1 mL) and 8 mL of Et_3OBF_4 were refluxed together for 9 days with 1 mL of additional nitrile added at two different intervals. The resulting solution was an intense orange color. Addition of CH_2Cl_2 yielded a very oily solid that was not well characterized. Further attempts to obtain a solid from the solution led only to oils.

(20) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with Pentanedinitrile

A sample of 2 (100 mg, 0.104 mmol) was stirred in 2 mL of warm NC(CH₂)₃CN which resulted in the production of a brown solution within several hours. Upon work-up consisting of addition of diethyl ether, the solution produced a brown solid whose ¹H NMR spectrum displayed the broad features indicative of a paramagnetic compound. Efforts to measure the infrared spectrum led to solids that did not mull well with Nujol, and KBr pellet samples that were not concentrated enough to register. The presence of [BF₄][•] was observed in the Nujol mull spectra, but the insignificant nitrile stretches were inconclusive as to the presence of coordinated dinitrile.

(21) Reaction of [Rh₂(MeCN)₁₀][TFMS]₄ with Pentanedinitrile

A small amount of 3 was dissolved in 3 mL of fresh $NC(CH_2)_3CN$ that was not deoxygenated. Stirring at room temperature initially produced a red solution then an orange-brown solution. Hexanes and diethyl ether layer attempts failed to mix with the reaction solution; toluene and CH_2Cl_2 did not precipitate any solid.

(22) Reaction of [Rh₂(MeCN)₁₀][BF₄]₄ with Propanedinitrile

A sample of 2 (50 mg, 0.052 mmol) was added to a small amount of NCCH₃CN. (This material is a highly toxic solid with a melting point of 32-34 °C, therefore it melts rapidly at warmer temperatures.) An internal finger condenser was used during the heating of this reaction which induced solidification of the malononitrile, and unfortunately, the addition of diethyl ether to lower the melting point resulted in the precipitation of a product. Subsequent washing with diethyl ether (5 x 5 mL) produced a dry red-brown solid. IR (CsI, Nujol), cm⁻¹: 3321 (s, br), 3259 (s, br), 2219 (s, br), 1661 (s), 1621 (s), 1597 (s), 1566 (s), 1062 (s, br). ¹H NMR (CD₃CN, in air, not wellphased) ppm: $\delta = 3.88(s)$, 3.76 (s) in *ca.* a 1 : 20 ratio.

(23) Conversion of [Rh₂(MeCN)₁₀][BF₄]₄ to Rh₂(OAc)₄(MeOH)₂

An amount of 2 (50.0 mg, 0.052 mmol) and an excess of NaOAc (80.8 mg, 0.985 mmol) were refluxed in glacial acetic acid for 1 h. The solution color quickly reverted from orange to green, and after cooling a blue solid formed which was removed by filtration and recrystallized from MeOH. The identity of the solid as $Rh_2(OAc)_4(MeOH)_2$ was confirmed by a comparison of its UV-visible spectrum in MeOH to that of an authentic sample of $Rh_2(OAc)_4(MeOH)_2$ (λ_{max} , 580 and 435 nm). Recrystallized yield: 9.9 mg, 37.6%.

(24) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents of NaOAc

A quantity of 2 (51 mg, 0.053 mmol) and anhydrous NaOAc (8.5 mg, 0.104 mmol, 1.96 equiv.) was stirred in 5 mL of MeCN and gently heated. The reaction solution remained orange with some undissolved NaOAc, and did not convert to red or purple, the characteristic colors of either pure $[Rh_2(OAc)_2(MeCN)_6]^{2+}$ or a mixture of that and the starting material.

In early reactions, the expected reddish-purple solutions resulted and the identity of cis- $[Rh_2(OAc)_2(MeCN)_6]^{2+}$ was verified spectroscopically. $\{\lambda_{max} = 525 \text{ nm}, IR (KBr, Nujol, air), \text{cm}^{-1}: 3591 (m, br), 3538 (m, br), 2355 (m), 2306 (m), 2278 (m), 1644 (w), 1552 (s), 1075 (vs, br), ¹H NMR (CD₃CN) ppm: <math>\delta = 2.53$ (s, 4H, equatorial CH₃CN), 2.17 (s, 1H), 2.03 (s, 2H, O₂CCH₃), 1.95 (s, free CH₃CN). Unfortunately, these reactions were not reproducible. Several instances of impure starting materials were found during that time period, so the apparent success of these reactions may be attributed to contamination of $[Rh_2(MeCN)_{10}][BF_4]_4$ with amounts of $[Rh_2(OAc)_2(MeCN)_6]^{2+}$.

(25) Reaction of [Rh₂(MeCN)₁₀][TFMS]₄ with 2 equivalents of NaOAc

A sample of 3 (51.1 mg, 0.042 mmol) and NaOAc \cdot 3H₂O (11.7 mg, .086 mmol, 2.05 equiv.) was dissolved in 5 mL of acetone. Stirring at r. t. initially produced a red solution, but within 30 min., the solution became brown. Prolonged reaction yielded an oily green solid and a red solution.

(26) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with NaO_2CCF_3

A quantity of 2 (50 mg, 0.052 mmol) and 11.7 mg of NaO_2CCF_3 (0.086 mmol, 1.65 equiv.) was stirred in 4 mL of MeCN for several days. The resulting orange solution was layered with 10 mL of diethyl ether to produce
a brown precipitate and a small quantity of green solid. The electronic spectrum of the filtrate did not agree with that of $[Rh_2(OAc)_2(MeCN)_6]^{2+}$ $(\lambda_{max} = 512 \text{ nm})$. The solution was decanted, the solid was washed with diethyl ether, and dried *in vacuo*. IR spectral data for the brown solid did not resemble that of the target complex, viz., $[Rh_2(O_2CR)_2(MeCN)_6]^{2+}$ in particular, there was an absence of a carboxylate stretch in the spectrum. (KBr, Nujol, air), cm⁻¹: 2340 (w), 2315 (w), 1070 (m), 1020 (m). The brown solid was redissolved in 5 mL of MeCN to yield an orange solution that eventually produced orange microcrystals.

(27) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ and $NaO_2CC_3H_7$

A sample of 2 (63 mg, 0.065 mmol) was dissolved in 5 mL of MeCN. To this was added 15 mg of sodium butvrate (0.014 mmol, 2.2 equiv.) suspended in 8 mL of MeCN after which the mixture was heated gently with stirring. The color of the solution was red-orange indicating incomplete reaction, therefore an additional 21 mg of $NaO_2CC_3H_7$ (0.191 mmol, 2.94 equiv.) was added. The solution then became purple, after which diethyl ether (15 mL) was added to precipitate a white solid from the purple solution. The solution was filtered and reduced to a purple residue by application of dynamic vacuum. This solid turned green after prolonged exposure to vacuum. ^{1}H NMR verified the product to be Rh₂(O₂CC₃H₇)₄. (CD₃OD) ppm: $\delta = 4.87$ (s), 2.03 (t, 2 H Rh₂O₂C<u>CH₂CH₂CH₃</u>), 1.94 (s, 0.5 H, RhNC<u>CH₃</u>), 1.43 (m, 2 H, $Rh_2O_2CCH_2CH_2CH_3$, 0.73 (t, 3 H, $Rh_2O_2CCH_2CH_2CH_3$) (This product consists of mostly the anhydrous species which is why the axial CH₃CN integrates to less than two.) IR (CsI, Nujol, air), cm⁻¹: 1661 (m), 1576 (vs), 1414 (s), 1316 (m), 1097 (m), 1076 (m, br), 801 (w), 667 (w), 456 (w). No nitrile stretches are observed.

(28) Reaction of [Rh₂(EtCN)₁₀][BF₄]₄ with 2 equivalents of [*n*-Bu₄N][OAc]

A quantity of 4 (40 mg, 0.036 mmol) was stirred with 2 equiv. of $[n-Bu_4N][OAc]$ (21.8 mg, 0.072 mmol) in 5 mL of EtCN. The acetate salt appeared to insoluble in this medium, therefore the solution was reduced to a residue under vacuum, whereupon 5 mL of acetone was added. A brown precipitate and a red-brown solution ensued. The solid was isolated by filtration of the solution in air. IR data did not indicate significant activity in the nitrile region implying that this was not either the cis or trans isomer of the target complex, $[Rh_2(OAc)_2(EtCN)_6]^{2+}$. IR (CsI, Nujol, air), cm⁻¹: 1576 (w), 1306 (m), 1033 (vs, br), 771 (w), 534 (s), 522 (s).

(29) Axial Substitution Reactions of $[Rh_2(MeCN)_{10}][BF_4]_4$ with Donor Solvents.

(i) Reaction with MeOH. A quantity of 2 (20 mg, 0.021 mmol) was stirred in 5 mL of MeOH for 8 h. While the solid did not dissolve appreciably, it nevertheless gradually changed from orange color to red as the axial MeCN groups were extracted and replaced by MeOH. The solution was removed by decantation, and the solid was dried *in vacuo*. IR (Nujol, CsI), cm⁻¹: 3409 (s, br), 2341 (s), 2317 (s), 1066 (s, br), 1027 (s, br), 522 (m), 454 (w).

(ii) Reaction with THF. A 20 mg sample of 2 (0.021 mmol) was stirred in 5 mL of THF for 8 h. The solid was insoluble in THF, but the powder eventually turned a more pale orange than the starting material. The solvent was decanted and solid was dried under vacuum. IR (Nujol, KBr), cm⁻¹: 3404 (w, br), 3305 (w), 2345 (s), 2316 (s), 1061 (s, br), 1034 (s).

(iii) Reaction with Acetone. An amount of 2 (20 mg, 0.021 mmol)
was stirred in 5 mL of acetone for 8 h. The solid was slightly soluble in
acetone, and gradually formed a pale green solution and an olive green solid.
The solution was decanted and the solid was dried under reduced pressure.
IR (Nujol, KBr), cm⁻¹: 2332 (w), 2311 (w), 1635 (w), 1057 (s, br), 1032 (s, br).

(30) Preparation of $Rh_2(aq)^{n+}$ (5)

A sample of 2 (100 mg, 0.104 mmol) readily dissolved in 10 mL of deoxygenated milli-q water, purified by the Millipore system from Waters Chromatography, to give a red solution. Under refluxing conditions with periodic pumping, the reaction color changed from red to purple to blue and finally to green after 8 h. The solution was heated as it was pumped to dryness to ensure complete reaction through removal of free acetonitrile from the system. The product obtained in this manner was a dry green solid. (Purity of the starting material from residual acetate sources is crucial as evidenced by numerous reactions that produced $Rh_2(OAc)_4(H_2O)_2$ which was verified by crystallography or by inability of the dissolved material to bind to a cation exchange column.) IR (Nujol, KBr), cm⁻¹: 3445 (s,br), 3325 (s,br), 3213 (s, br), 1661 (s), 1597 (s), 1088 (s, br), 722 (s).

(31) Crystallization attempt of Rh₂(aq)⁴⁺

The *p*-toluenesulfonic acid that was used in this experiment was obtained from Fluka- The Aldrich samples of this reagent contain significant amounts of HCl. After preparing the green aqua complex, **5**, by the above method, the solution was transferred to a Dowex cation-exchange column containing *ca*. 2 cm^3 of resin that had been washed with *ca*. 30 mL of pure H₂O. The Rh-containing solution was then applied to the column; a green

band remained bound to the resin and was washed with several 5 mL portions of water. The column and the new receiving flask were deoxygenated by a N₂ purge for several hours as was the 4 <u>M</u> solution of *p*toluenesulfonic acid. The green compound was eluted easily by anaerobic transfer of the acid. The resulting solution was evaporated under a nitrogen purge. While large amounts of the acid crystallized, no green crystals of the $Rh_2(aq)^{4+}$ species were observed. The solution did not totally evaporate, and the product was still dissolved in the acidic solution.

(32) Conversion of $Rh_2(aq)^{4+}$ to $Rh_2(OAc)_4$

Quantities of 5 (20 mg) and excess NaOAc (37 mg, 0.449 mmol) were dissolved in 10 mL of glacial acetic acid and heated for 12 h. The resulting blue precipitate was identified as $Rh_2(OAc)_4$ by the UV-visible spectrum (*vide supra*).

(33) Aerobic Reaction of $[Rh_2(McCN)_{10}][BF_4]_4$ with Water at Room Temperature

A quantity of $[Rh_2(MeCN)_{10}][BF_4]_4$ (24.5 mg, 0.025 mmol) was dissolved in 4 mL of H₂O in air. After 20 min., the solution was orange with a hint of red ($\lambda_{max} = 503$ nm). Within 21 h, the solution had changed to orange-brown, (UV-visible shoulder at 523 nm). The solution was allowed to stand for two weeks, after which the color was a very pale yellow. The solvent was removed under vacuum to yield a green residue. This solid was dissolved in water to give a yellow solution with a $\lambda_{max} = 548$ nm. ¹H NMR (CD₃CN), gave a large number of resonances superimposed on a broad feature between 2.0 and 2.8 ppm. The presence of free CH₃CN was apparent at $\delta = 1.95$ ppm.

(34) Reaction of Rh₂(aq)ⁿ⁺ with Acetonitrile

Dissolution of **5** in MeCN with heating produced a red solution that did not revert to an orange color that is characteristic of $[Rh_2(MeCN)_{10}]^{4+}$ (λ_{max} = 506 nm). IR spectral data reveal only very tiny v(C=N) and intense v(OH) stretches- (KBr, Nujol), cm⁻¹: 3377 (vs, br), 2333 (vw), 2302 (vw), 2273 (vw), 1622 (m, br), 1053 (vs, br).

(35) Reaction of [Rh₂(MeCN)₁₀][BF₄]₄ with HClO₄

A 20 mg sample of 2 (0.021 mmol) was refluxed in 5 mL of 3 <u>M</u> HClO₄ for *ca.* 12 h. The pale green solution was transferred anaerobically to a quartz UV-visible cell and the spectrum was recorded. Once the visible spectrum had been measured, the solution was exposed to air. After seven days, the solution had displayed no signs of decomposition.

(36) Preparation of a UV-visible sample of $Rh_2(aq)^{n+}$ in 3 <u>M</u> HClO₄

A residue left from a preparation of 5 in H_2O was redissolved in fresh H_2O and loaded onto a cation exchange column. The column was purged with nitrogen for several hours, and the compound was eluted anaerobically with 3 <u>M</u> HClO₄.

(37) Control reaction of Rh₂(OAc)₄(MeOH)₂ in Water

 $Rh_2(OAc)_4(MeOH)_2$ (50 mg, 0.099 mmol) was refluxed in 5 mL of H_2O for three days. While a minor amount of rhodium metal was produced, the dirhodium tetraacetate molecule was essentially unchanged as evidenced by the its visible spectrum ($\lambda_{max} = 586$ and 441 nm).

(38) Reaction of Rh₂(OAc)₄(MeOH)₂ with Et₃OBF₄ and Pyridine

An amount of Rh₂(OAc)₄(MeOH)₂ (200 mg, 0.395 mmol) was refluxed with 8 mL Et₃OBF₄ in 5 mL of pyridine for 4 days. A pink solid precipitated from the orange solution. Decanting followed by reduction of the volume of the orange solution and addition of CH₂Cl₂ yielded a large amount of yellow precipitate. Crystals of the yellow precipitate were grown and examined by X-ray crystallography, but these proved to be twinned. IR (CsI, Nujol, air), cm⁻¹: 3287 (s), 3202 (s), 3147 (s), 3118 (s), 1638 (s), 1609 (s), 1540 (s), 1216 (m), 1067 (vs, br), 763 (s), 750(s), 697 (s), 679 (s), 510 (m). ¹H NMR (CD₂Cl₂), ppm: δ = 8.48 (d), 8.06 (t), 7.44 (t), 5.32 (d), 3.39 (s), 1.14 (t). The pink solid was insoluble in all common solvents including pyridine; yield, 336 mg. IR (KBr, Nujol), cm⁻¹: 3448 (vs), 3400 (vs), 3095 (s), 1635 (vs), 1582 (m), 1498 (vs), 1302 (s), 1188 (vs), 1075 (vs, br), 785 (s), 697 (s), 575 (s), 477 (m).

(39) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with Pyridine

A sample of 2 (86 mg, 0.089 mmol) was stirred at r. t. in 5 mL of pyridine that had been freeze-pump-thawed over 4Å molecular sieves to remove residual oxygen and water. The reaction was covered with aluminum foil and allowed to react for three days. After this time, the stirring was halted, and the solution, which had appeared to be orange, was merely a suspension of the starting material in the solvent.

(40) Reaction of [Rh₂(MeCN)₁₀][TFMS]₄ with Pyridine

A sample of 3 (25 mg, 0.021 mmol) was stirred in 3 mL of pyridine that had been freeze-pump-thawed to remove residual oxygen. The solution immediately turned bright yellow. When stirring was ceased, a small amount

of solid settled out, therefore 4 mL of additional pyridine was added. The solid did not dissolve even with warming. Subsequently, 5 mL of CH_2Cl_2 was layered under the pyridine solution in an attempt to crystallize the product. A large amount of solid was produced which when redissolved in MeCN, became a deep red-brown color. By layering hexanes and diethyl ether on this solution, olive green feathery crystals and a yellow solution were obtained. No spectral characterization was carried out.

(41) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents of Bipyridine in Acetonitrile

Quantities of 2(100 mg, 0.104 mmol) and bpy (33 mg, 0.212 mmol, 2.04 equiv.) were dissolved separately in 5 mL MeCN each and combined by cannula transfer of the second solution into the first. The combined solution immediately turned dark green with a small amount of flocculent precipitate. Addition of diethyl ether produced a brown solid, and chilling to -40 ∞ precipitated the entire contents of the solution. The solvent was decanted to give a brown solid admixed with white microcrystals. This residue was dried under vacuum and then redissolved in 5 mL of MeCN to give a red solution and a brown suspension. The vessel was wrapped in aluminum foil, filtered by cannula without exposure to light, and dissolved in MeCN. The solution was layered over CH_2Cl_2 which produced a powdery olive green solid and an orange solution. The solid was collected by cannula filtration and dried in vacuo. IR(CsI, Nujol), cm⁻¹: 2362 (w), 2334 (m), 1610 (w), 1577 (w), 1320 (w), 1248 (w), 1058 (vs, br), 768 (m), 523 (m). ¹H NMR (CD₃CN), ppm: $\delta = 8.69$ (d, 2H), 8.44 (m, 2.5H), 7.70 (m, 4H), 5.43 (s, .6H), 2.82 (s, .5H), 1.95 (s, ~15H). The orange solution was reduced to a mixture of orange and white solids under vacuum. IR(CsI, Nujol, very dilute), cm⁻¹: 1059 (s. br). ¹H NMR

 (CD_3CN) , ppm: $\delta = 8.68$ (d, 2H), 8.43 (t, 3H), 7.68 (m, 6H), 7.19 (m, 2H), 5.44 (s, 0.5H), 3.26 (s, 2H), 2.65 (s, 2H), 1.95 (s, ~ 50H).

(42) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents of Bipyridine in acetone

Samples of 2 (82 mg, 0.085 mmol) and bpy (21 mg, 0.134 mmol, 1.56 equiv.) were dissolved separately in about 5 mL of acetone each and then the bpy solution was transferred under N₂ into the Rh-containing solution. A finely divided gray suspension immediately resulted. After stirring overnight, there was a large amount of gray precipitate and a very pale orange solution. The solution was decanted and discarded. After the gray solid had been washed with MeCN, it dissolved to give an olive solution with a gray suspension. The solution was reduced to a residue under vacuum, and a ¹H NMR in CD₃CN displayed only free MeCN at $\delta = 1.95$ ppm.

(43) Reaction of [Rh₂(EtCN)₁₀][BF₄]₄ with 2 equivalents of Bipyridine

Quantities of 4 (74 mg, 0.067 mmol) and bpy (21 mg, 0.135 mmol, 2.01 equiv.) were dissolved separately in *ca*. 3 mL of CH₃NO₂ each. The bpy solution was transferred anaerobically by cannula into the rhodium solution which immediately changed from orange to red-brown. The reaction was stirred for two hours, after which the solution was layered with hexanes and diethyl ether (1 mL and 10 mL respectively). After 5 days, this had produced an orange solution and an oily green-black product similar in color to the product from $[Rh_2(MeCN)_{10}][BF_4]_4$ with 4 equiv. of bpy. The solution was decanted from the solid, which was washed with diethyl ether (3 x 5 mL) and dried *in vacuo* to isolate a dry forest green powder. ¹H NMR (CD₃NO₂),ppm: $\delta = 8.81$ (d, 2H, bpy), 8.51 (t, 2H, bpy), 7.92 (d, 2H, bpy), 7.78 (t, 2H, bpy), 4.35 (s, 1H, free CH_3NO_2). Additional multiplets appear in the baseline between 1.0 and 3.5 ppm which are attributed to free EtCN.

(44) Reaction of [Rh₂(MeCN)₁₀][BF₄]₄ with 4 equivalents of Bipyridine

Amounts of 2 (100 mg, 0.104 mmol) and bpy, (65 mg, 0.416 mmol, 4.0 equiv.) were combined. To this mixture was added 5 mL of CH₃NO₂. Rapid color changes ensued: red to green to brown to purple to green to finally teal, all within ~ 2 min. 24 h after no further color changes had been observed, the solution was layered with diethyl ether (10 mL). The solution was decanted from the gray-black solid. After washing with diethyl ether (2 x 5 mL), the solid was still very sticky. Subsequent washing with CH₂Cl₂ and THF did not improve the nature of the oily residue. The solid was redissolved in CH₃NO₂, to which diethyl ether was added, and the flask was chilled to 0 °C. The solution was then decanted, and the solid was dried *in vacuo*. IR(CsI, Nujol), cm⁻¹: 2332 (w), 2307 (w), 1608 (w), 1554 (w), 1502 (w), 1321 (w), 1284 (w), 1250 (w), 1059 (vs, br), 767 (m), 520 (m). ¹H NMR (d⁶-acetone) ppm: δ = 9.05 (d), 8.60 (t), 8.25 (d), 7.88 (t), 4.42 (s).

(45) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents of dppm

Samples of 2 (100 mg, 0.104 mmol) and dppm (80 mg, 0.208 mmol, 2.0 equiv.) were stirred at r. t. in *ca.* 7 mL freshly distilled MeCN. The solution immediately turned an intense ruby red color. After ~ 2 h, the solution darkened in color and a brown solid was seen to be suspended in the solution. A dark brown solid was precipitated from the reaction solution by the addition of 10 mL of diethyl ether. A ¹H NMR spectrum in d⁶-acetone and CD₃CN displayed no proton resonances in the phenyl region.

(46) Reaction of [Rh₂(MeCN)₁₀][TFMS]₄ with 2 equivalents of dppm

A small amount of 3 (20 mg, 0.017 mmol) was stirred at r. t. in 5 mL of acetone together with 13 mg of dppm (0.034 mmol, 2.0 equiv.). The solution immediately turned a bright orange-red. After 90 min., hexanes and diethyl ether were layered on the solution. Three days later, a few small yellow crystals had formed. Attempts to produce any more compound by layering with toluene met with failure.

In a separate reaction, samples of $[Rh_2(MeCN)_{10}][TFMS]_4$ (53 mg, 0.044 mmol) and dppm (33 mg, 0.086 mmol, 1.95 equiv.) were dissolved in 6 mL of acetone and 3 mL of acetone respectively before being combined under anaerobic conditions. The color of the combined solution remained that of the original Rh₂ starting material.

(47) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 2 equivalents of PMe₃

A sample of 2 (50 mg, 0.052 mmol) and 0.1 mL of a 1 <u>M</u> solution of PMe₃ (0.100 mmol, 1.93 equiv.) in toluene was stirred at r. t. in 5 mL of MeCN for 1 day. The solution immediately turned ruby-red, went through a dark brown phase, and after 1 more day was once again the pale orange of the starting material with a white precipitate at the bottom. This reappearance of the original solution color indicated that the original compound had reformed.

(48) Reaction of [Rh₂(MeCN)₁₀][BF₄]₄ with ppnCl

Samples of 2 (100 mg, 0.104 mmol) and 238 mg of ppnCl (0.415 mmol, 3.99 equiv.) were stirred at r. t. for ~ 12 h. Immediately after addition of the solvent, the solution turned gray-white with a dingy white precipitate. The

next morning, the solution was decanted and allowed to evaporate, producing a large amount of white crystals. The precipitate from the reaction was washed with 20 mL of MeCN. The compound was insoluble in THF and CH_2Cl_2 but was quite soluble in water. This reaction was not reproducible. In all subsequent chloride reactions, the solutions remained pale orange and formed no precipitate.

(49) Crystallization of an oxygen derivative of $[Rh_2(MeCN)_{10}][BF_4]_4$

An amount of $[Rh_2(MeCN)_{10}][BF_4]_4$ was dissolved anaerobically in MeCN and then covered with foil for an hour. O₂ was bubbled for 15 min. after which CH₂Cl₂ was layered under the solution. Orange block-shaped crystals resulted and were examined on an X-ray diffractometer. These proved to exhibit the same unit cell as an authentic sample of $[Rh_2(MeCN)_{10}][BF_4]_4$.

(50) Long term reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with O₂ and hv

A sample of 2 (22 mg, 0.023 mmol) was dissolved in 30 mL of MeCN and purged with O_2 during irradiation with a broad band UV-visible source for 3 days after which the solution was yellow. The volume of the solution was reduced and layered with hexanes (2 mL) and ether (20 mL). A yellow oil was produced; unfortunately subsequent attempts to isolate a solid led only to further oiling of the solution.

C. Experimental, Crystallography

1. $[Rh_2(MeCN)_{10}][BF_4]_4$ (2)

Data Collection. Pertinent crystal data are summarized in Table 5. Large orange block-shaped crystals were obtained from the reaction solution; one of these with dimensions $0.75 \ge 0.78 \ge 0.80$ mm was mounted with epoxy cement on the end of a glass fiber. The crystal was examined on a Nicolet P3/F diffractometer with graphite monochromated MoK α ($\lambda \alpha = 0.71073$ Å) radiation. A rotational photograph indicated that the crystal diffracted well. The unit cell was determined by 25 reflections in the range $20 \le 2\theta \le 30^{\circ}$. The crystal indexed in the monoclinic crystal system which was verified by axial photography.

Structure Solution and Refinement. The intensity of three periodically monitored check reflections decayed by ~40% thus the program CHORT was applied to compensate for this loss of intensity. The position of the unique Rh atom was determined by application of SHELXS-86,⁵ and the rest of the atoms were located by an alternating series of least squares refinement and difference Fourier maps. Anisotropic refinement of all non-hydrogen atoms gave residuals of R = 0.0520 and R_w = 0.0807 with the quality-of-fit index equal to 2.33. In the last cycle, 235 parameters were refined with 2802 unique data and F_{obs}>3 σ of 2395. The shift/esd of the final cycle was 0.13 and the highest remaining peak in the final difference Fourier map was $1.7 \text{ e}^{-}/\text{Å}^3$.

2. [Rh₂(MeCN)₁₀][TFMS]₄ (3)

Data Collection. X-ray quality crystals were grown by layering a solution of 3 that had been standing in the dark for at least 90 min. with

Formula	Rh ₂ C ₂₀ H ₃₀ N ₁₀ B ₄ F ₁₆
Formula weight	963.51
Space group	C2/c
a, Å	18.123(2)
b, Å	11.920(1)
с, А	18.243(3)
α, deg	90
β, de g	99.58(1)
γ, deg	90
V, Å ³	3886(1)
Z	4
d _{calc, g/cm} 3	1.647
μ (Mo Kα), cm ⁻¹	9.383
Data collection instrument	Nicolet P3/F
Radiation (monochromated in incident beam)	Mo K $\alpha(\lambda \alpha = 0.71073 \text{\AA})$; graphite monochromated
Temperature, °C	23 ± 2°
Scan method	θ - 2θ
Trans. factors, max., min.	98.8, 8 7.9 %
Ra	0.0520
R _w ^b	0.0807
$aR = \Sigma F_0 - F_c / \Sigma F_0 $	

Table 5. Crystal Data for $[Rh_2(MeCN)_{10}][BF_4]_4$ (2)

 $bR_{w} = [\Sigma w |F_{o}| - |F_{c}|)^{2} / \Sigma w |F_{o}|^{2}]^{1/2}; w = 1/\sigma^{2}(|F_{o}|)$

hexanes and diethyl ether. The flask was covered with foil for the duration of the diffusion experiment. A crystal of approximate dimensions $0.54 \ge 0.39 \ge 0.39 \le 0.39 \le$

Structure Solution and Refinement. The structure was solved by the direct-methods program, SHELXS-86 which led to location of the two Rh atoms. The rest of the structure was determined by a series of alternating DIRDIF and Fourier maps until the majority of the atoms had been found. Least-squares analysis and Fourier maps were used to complete the structure. After isotropic convergence was achieved, the program, DIFABS was applied to correct for absorption. The four CF₃ groups did not refine well as individual atoms, so the three atoms were refined together as a group. All atoms other than these groups and the interstitial MeCN solvent molecule were refined aniostropically to give final residuals of R = 0.075 and Rw = 0.091 with the quality-of-fit indicator equal to 2.35. A final difference map gave the highest remaining peak as $1.5 \text{ e}/\text{Å}^3$, located in the lattice. All other peaks were less than $1.0 \text{ e}/\text{Å}^3$.

Formula	$Rh_2C_24H_{30}N_{10}S_4O_{12}F_{12}$
Formula weight	1212.578
Space group	P21/n
a, Å	12.195(8)
b, Å	22.797(3)
c, A	18.686(3)
α, deg	90
β, deg	97.57(2)
γ, deg	90
V, Å ³	5150(3)
Z	4
d _{calc, g/cm³}	1.616
μ (Mo Kα), cm ⁻¹	8.87
Data collection instrument	Nicolet P3/F
Radiation (monochromated in incident beam)	Mo K $\alpha(\lambda \alpha = 0.71073 \text{\AA})$; graphite monochromated
Temperature, °C	-90 ± 2°
Scan method	θ - 2 θ
Trans. factors, max., min.	0.89 - 1.11
Ra	0.075
R _w ^b	0.091
$\mathbf{aR} = \Sigma F_0 - F_c /\Sigma F_0 $	

 ${}^{b}R_{w} = [\Sigma w |F_{o}| - |F_{c}|)^{2} / \Sigma w |F_{o}|^{2}]^{1/2}; w = 1/\sigma^{2}(|F_{o}|)$

3. $[Rh_2(EtCN)_{10}][BF_4]_4$ (4)

Data Collection. Large single crystals of 4 were grown by placing a layer of hexanes on the reaction solution and layering diethyl ether on top of this. Slow diffusion produced hexagonal rod-shaped crystals. A crystal of dimensions $0.31 \ge 0.36 \ge 0.89$ mm was mounted on a glass fiber and examined on a Rigaku AFC6S diffractometer equipped with graphite monochromated Mo K α ($\lambda \alpha = 0.71073$ Å) radiation. A random search routine located initial reflections to determine a cell. The pre-cell was determined by 25 reflections with $29 \le 2\theta \le 30$, and the symmetry was confirmed as monoclinic C-centered by an automatic Laue check. Data were collected to a maximum 20 value of 50° at -90 °C. Three intensity standards collected every 150 reflections displayed no significant decay. Pertinent crystal data are summarized in Table 7.

Structure Solution and Refinement. The structure was solved by application of direct methods. The unique Rh atom and immediate coordination sphere were located from the initial solution whereas all other non-hydrogen atoms were located and refined from a series of alternating least squares and difference Fourier maps. Two reflections were found to be extremely poor fits to the model, therefore these were eliminated from the calculations. The program, DIFABS, was applied to correct for absorption problems. Two of the ethyl groups were disordered, therefore two orientations were each refined at half occupancy. All atoms were refined anisotropically. Final refinement gave residuals of R = 0.047 and $R_w = 0.072$ with the quality-of-fit indicator = 2.27. The last cycle refined with 316 parameters and 3353 data with $F_{obs} > 3\sigma$; the maximum shift/esd was 0.05, and a final difference Fourier showed the highest peak to be 1.04 e⁻/Å³ in the map.

Table 7. Crystal Data for $[Rh_2(EtCN)_{10}][BF_4]_4$

Formula	Rh ₂ C ₃₀ H ₅₀ N ₁₀ B ₄ F ₁₆
Formula weight	1103.82
Space group	C2/c
a. A	19.920(4)
b, A	12.646(2)
c, A	18.646(2)
α, deg	90
β, d eg	92.55(2)
γ, deg	90
V, A ³	3886(1)
Z	4
d _{calc, g/cm³}	1.574
μ (Mo Kα), cm ⁻¹	7.93
Data collection instrument	Rigaku AFC6-S
Radiation (monochromated in incident beam)	Mo K $\alpha(\lambda \alpha = 0.71073 \text{Å})$; graphite monochromated
Temperature, °C	-90 ± 2°
Scan method	$\omega = 2\theta$
Rª	0.047
R _w b	0.072
$aR = \Sigma F_0 - F_c / \Sigma F_0 $	

 $bR_{w} = [\Sigma w | F_{o} | - | F_{c} |)^{2} / \Sigma w | F_{o} |^{2}]^{1/2}; w = 1/\sigma^{2} (|F_{o}|)^{2}$

D. Results and Discussion

$[Rh_2(MeCN)_{10}][BF_4]_4$

Synthesis

Preparation of fully solvated dirhodium cation species has been established by several routes. The first successful method employed triethyloxonium tetrafluoroborate as an alkylating reagent to remove the carboxylates from rhodium tetraacetate. This reaction is done in excess of the oxonium reagent

$$Rh_{2}(OAc)_{4}(MeOH)_{2} + [Et_{3}O][BF_{4}] \xrightarrow{\Delta} MeCN$$

$$10 \text{ days} \qquad [Rh_{2}(MeCN)_{10}][BF_{4}]_{4}$$

$$60-70\% \text{ Yield}$$

Equation 7

to drive the reaction to completion mainly because of a competing side reaction of Et₃OBF₄ with MeCN which yields the iminium salt, [MeCNEt]+[BF₄]⁻. This preparative method involves a rather long reaction time (up to two weeks) and maximizing the yield is tedious due to a propensity of the reaction solutions to produce oils. Shorter reaction times, addition of CH₂Cl₂, and lower temperatures yield a mixture of the desired product with the [Rh₂(OAc)₂(MeCN)₆]²⁺ complex. Incomplete reaction occurs most often when excessive CH₂Cl₂ is present because the intermediate precipitates and does not redissolve to undergo further reaction. The product mixtures often appear red by casual examination, but careful scrutiny reveals the presence of admixed purple and orange crystals. The mixtures are easily identified by ¹H NMR spectroscopy where the resonances at $\delta = 2.31$ and $\delta =$ 2.03 ppm appear for the intermediate; large amounts of this impurity may be observed in the IR spectrum as four bands in the v(C=N) region between 2340 and 2249 cm⁻¹ due to the spectral overlap of the two compounds. No sign of either a tris-acetate or a mono-acetate intermediate was detected, suggesting that the bridging ligands are removed in pairs and cis to each other.

A second successful strategy for the synthesis of $[Rh_2(MeCN)_{10}][BF_4]_4$ was found from the reaction of tetrafluoroboric acid with $Rh_2(OAc)_4(MeOH)_2$. The acid protonates the carboxylates, liberating acetic acid. Solvent replaces the vacant coordination sites as in the equation below:

$$Rh_{2}(OAc)_{4}(MeOH)_{2} + HBF_{4} \cdot Et_{2}O \xrightarrow{MeCN} [Rh_{2}(MeCN)_{10}][BF_{4}]_{4}$$
protonation
$$60-70\% \text{ Yield}$$

Equation 8

This reaction proceeds slightly faster than the triethyloxonium method, and high yields of the crystalline product may be achieved by layering hexanes and diethyl ether on top of the reaction solution. The product must be recrystallized once again prior to use, nevertheless this procedure has proved to be a very convenient method for accessing the solvated compound in relatively high yields.

Spectroscopy

The ¹H NMR spectrum of **2** displayed rather surprising results. If the salt is recrystallized in the dark, one observes only one resonance at $\delta = 1.95$ ppm for free MeCN indicating that all the solvent ligands have exchanged for CD₃CN. If the solid is recrystallized in room light or if the sample is

prepared in air, a second resonance at $\delta = 2.65$ ppm appears in a ratio of about 4:1 with the 1.95 resonance. (See Figures 10 and 11) The former resonance was initially mistaken as a resonance for the equatorial ligands in $[Rh_2(MeCN)_{10}]^{4+}$, but it appears more likely that it is due to an impurity that co-crystallizes with $[Rh_2(MeCN)_{10}][BF_4]_4$. In studies of the pure crystals grown in the dark, we were not able to record a spectrum containing bound solvent within the time constants of sample preparation and setting up the experiment. A sample prepared anaerobically and immediately purged with O₂ displays an intermediate amount of the $\delta = 2.65$ ppm resonance. The extremely rapid ligand exchange from all positions in the pure crystals contradicts the postulation of Chisholm and Cayton who suggested that $Rh_2(II,II)$ species should be relatively substitutionally inert in the equatorial positions.⁶

The infrared spectrum of $[Rh_2(MeCN)_{10}][BF_4]_4$ displays a large broad feature centered around 1065 cm⁻¹ due to the $[BF_4]^-$ stretches. The most sensitive region for identification is the v(C=N) region (2345, 2315, and 2287 cm⁻¹); these are in order of decreasing intensity. These three features are predicted by group theory treatment of an idealized D_{4h} molecule. The lowest intensity

stretch is due solely to the axial ligands since this band is absent in solution spectra, while the other two stretches remain unchanged (2342, 2317 cm⁻¹). A solution spectrum in CD₃CN helped identify the remaining two stretches as v(C=N) and the CH₃ deformation/C-C stretching combination mode. The infrared data in solution show a greatly reduced intensity of the highest energy band (2361, m), an intense intermediate energy band (2334, vs), a weaker lower energy band (2307 w), and a new feature at 2112 due to the

Figure 10. ¹H NMR spectrum of [Rh₂(MeCN)₁₀][BF₄]₄ recrystallized in the absence of light

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Figure 10

Figure 11. ¹H NMR spectrum of [Rh₂(MeCN)₁₀][BF₄]₄ recrystallized in the presence of light

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Figure 11

exchanged CH₃CN. The latter is unobservable in other solution spectra since the experiments are carried out in CH₃CN. The exact position of the bands has shifted slightly, presumably due to the remote isotope effect on the force constants, however the pattern of three bands remains the same suggesting that the stretches still parallel those of the protic solvent spectrum. This particular solid sample was recrystallized in room light and thus is likely to undergo solvent exchange at a much slower rate as verified by ¹H NMR experiments, so the incomplete disappearance of some stretches is understandable. Still, this is enough evidence to assign the three features of the protic samples in this region: the highest energy band around 2350 cm⁻¹ is the combination mode due to CH₃ deformation and C-C stretching, the center band around 2315 cm⁻¹ is the v(C=N) of the coordinated equatorial ligands, and the last is due to the axial ligands.

Surprisingly, complete solvent exchange does not appear to take place in CH₃NO₂. Solution infrared spectra show that the stretches of the equatorial ligands do not change (2342 vs, 2314 s) while a single additional band appears at 2254 cm⁻¹ which is apparently the solvent that is exchanged from the axial positions. A ¹H NMR spectrum of [Rh₂(MeCN)₁₀][BF₄]₄ in CD₃NO₂ displays two resonances, one singlet at $\delta = 2.74$ ppm due to equatorial MeCN, and a very broad feature at $\delta = 2.42$ ppm attributed to the exchanged axial groups. This spectrum is invariant over the course of 7 days. The breadth of the resonance at 2.42 ppm indicates rapid exchange is occurring at the axial sites. Apparently nitromethane is sufficiently polar to dissolve the tetracation, but competes poorly for all but axial coordination sites.

Electronic spectra of anaerobic solutions of $[Rh_2(MeCN)_{10}]^{4+}$ prepared in the dark display two absorptions, one at $\lambda_{max} = 468$ nm and a second

feature at 270 nm. The influence of light on these spectra will be discussed in Chapter IV. A cyclic voltammogram of $[Rh_2(MeCN)_{10}][BF_4]_4$ in 0.1 <u>M</u> TBABF₄ in MeCN displays a single irreversible reduction at $E_{p,c} = -0.05V$ vs Ag/AgCl (-0.538V vs. Fc/Fc+). The absence of an accessible oxidation, which is usually observed for Rh₂(II,II) species,¹ is not surprising due to the high charge localized on the metal centers.

Molecular Structure

A summary of selected bond distances and angles are presented in Tables 8 and 9. Positional parameters are included in the Appendix. The ORTEP diagram in Figure 12 clearly shows the dirhodium unit with each metal in an octahedral environment consisting of five ligands with the sixth position being occupied by the other metal. The center of the Rh-Rh bond resides on a crystallographic C₂ axis. The equatorial planes of CH₃CN ligands are twisted with respect to each other with a torsion angle χ_{av} of 44.8°. The axial CH₃CN groups deviate somewhat from linearity which reduces the molecular symmetry from the idealized D_{4d} to C₂. This essentially perfectly staggered arrangement (depicted in Figure 13) reflects the low steric demand of acetonitrile as a ligand. The few previously reported unbridged dinuclear rhodium compounds that have been structurally characterized exhibit torsional twist angles less than 45° due presumably to the bulky size of the ligands as in Rh₂(dmg)₄(PPh₃)₂, $\chi = 42.6^{\circ}$,⁷ (dmg = dimethylglyoximate anion) and Rh₂(p-CH₃C₆H₄NC)₈I₂²⁺, $\chi = 26^{\circ}$.⁸

While this is not the first example of an unbridged Rh-Rh bond, it represents a rare example of this unit in the absence of any significant repulsion between ligands. The longest distance for a Rh(II)-Rh(II) bond to date is 2.936 Å found in the Rh₂(dmg)₄(PPh₃)₂⁷ molecule in which the

Table 8	Selected Bond	Distances in	Å for [Rho(MeCN)10][BF4]4
1 able 8.	Selected Dona	Distances in	A for [Itil2(meOit)]0][D14]4

Atoml	Atom2	Distance
Rh(1) Rh(1) Rh(1) Rh(1) Rh(1) Rh(1) N(1) N(1) N(2) N(3) N(4) N(5) C(1) C(3) C(5) C(7) C(9) B(1) B(1) B(1) B(2) B(2) B(2)	Rh(1)' N(1) N(2) N(3) N(4) N(5) C(1) C(3) C(5) C(7) C(2) C(2) C(2) C(4) C(6) C(2) C(4) C(6) C(10) F(1) F(2) F(3) F(4) F(5) F(6) F(7)	2.624(1) 1.986(4) 1.980(4) 1.995(4) 2.191(5) 1.131(5) 1.159(6) 1.117(6) 1.140(6) 1.139(8) 1.460(7) 1.429(7) 1.485(7) 1.485(7) 1.485(7) 1.485(7) 1.485(7) 1.372(10) 1.291(9) 1.362(11) 1.372(12) 1.340(9) 1.271(8) 1.283(9)
2(2)	. (0)	1.57(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

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Table 9. Selected Bond Angles in degrees for $[Rh_2(MeCN)_{10}][BF_4]_4$

Atoml	Atom2	Atom3	Angle
Rh(1)' Rh(1)' Rh(1)' Rh(1)' Rh(1)' N(1) N(1) N(1) N(1) N(1) N(2)	Rh(1) Rh(1) Rh(1) Rh(1) Rh(1) Rh(1) Rh(1) Rh(1) Rh(1) Rh(1)	N(1) N(2) N(3) N(4) N(5) N(2) N(3) N(4) N(5) N(5)	90.2(1) 87.5(1) 90.5(1) 90.1(1) 178.1(1) 89.0(1) 178.7(1) 91.9(2) 88.7(2)
N(2)	Rh(1)	N(3)	177 4(2)
N(2)	Rh(1)	N(5)	94.1(2)
N(3)	Rh(1)	N(4)	89.2(2)
N(3)	Rh(1)	N(5)	90.6(2)
N(4) Ph(1)	Rn(1) N(1)	N(5)	88.4(2) 176 2(A)
Rh(1)	N(1) N(2)	C(1)	174.4(4)
Rh(1)	N(3)	C(5)	176.7(4)
Rh(1)	N(4)	C(7)	176.2(4)
Rh(1)	N(5)	C(9)	166.1(5)
N(1) N(2)	C(1)	C(2)	175.9(5)
N(3)	C(5)	C(6)	177.9(6)
N(4)	C(7)	C(8)	177.2(6)
N(5)	C(9)	C(10)	178.4(7)
F(1)	B(1) B(1)	F(2)	120.(1) 115.7(7)
F(1)	B(1)	F(4)	103.6(7)
F(2)	B(1)	F(3)	111.3(6)
F(2)	B(1)	F(4)	100.6(9)
F(3)	B(1)	F(4)	102.(1)
F(5) F(5)	B(2) B(2)	F(0)	115.0(0) 120.2(7)
F(5)	B(2)	F(8)	96.(1)
F(6)	B(2)	F(7)	123.9(7)
F(6)	B(2)	F(8)	97.(1)
F(7)	B(2)	F(8)	72.3(8)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Figure 12. ORTEP diagram of the cationic component of [Rh₂(MeCN)₁₀][BF₄]₄ viewed perpendicular to the Rh-Rh bond

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Figure 13. ORTEP diagram of the solvated cation of [Rh₂(MeCN)₁₀][BF₄]₄ viewed parallel to the Rh-Rh bond depicting the staggered nature of the molecule

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equatorial ligands are close to achieving the maximum torsion angle, but the added presence of bulky axial PPh₃ groups prevent the ligands from further relieving steric repulsion by bending away from each other; as a result, the metal-metal distance lengthens. The Rh-Rh separation in $[Rh_2(MeCN)_{10}][BF_4]_4$ of 2.624(1)Å is much shorter than the other unbridged examples, but is still longer than the average length of 2.35-2.45 Å in tetra-bridged systems.⁹ It must be noted that the bridged systems generally employ anionic π -donors as ligands in contrast to the neutral σ -donors in this situation, so comparisons must necessarily be limited.

[Rh₂(MeCN)₁₀][TFMS]₄

Synthesis

Tetrafluoroborate salts display only limited solubility in common solvents. The $[Rh_2(MeCN)_{10}][BF_4]_4$ complex is completely insoluble in THF, CH_2Cl_2 , acetone, and alcohols, and dissolves only in MeCN, water, CH_3NO_2 , and other polar solvents such as DMSO. This limited range of solubilities serves to restrict subsequent reaction conditions, so preparation of a more soluble form of the salt was required. The most straightforward method of achieving this would be to exchange the anion by simple metathesis. Efforts to substitute *p*-toluenesulfonate for the $[BF_4]^-$ led to incomplete exchange as judged by the FT-IR spectrum which exhibited a substantial $[BF_4]^-$ stretch but no features due to the incoming anion. Metathesis did occur with LiTFMS as verified by the IR spectrum which displayed stretches typical for uncoordinated TFMS⁻ v[SO_3(E)] and v[SO_3(A_1)] at 1270 and 1043 respectively, and v[CF_3(A_1)] and v[CF_3(E)] at 1237 and 1167 cm⁻¹ respectively.¹⁰ The band near 1280 cm⁻¹ for ionic CF_3SO_3⁻ generally shifts to higher energy around 1380 cm⁻¹ for monodentate coordination of the anion. The characteristically broad $[BF_4]^-$ stretch at *ca*. 1070 cm⁻¹ was absent. Unfortunately, the new Rh salt and the original LiTFMS exhibit virtually identical solubilities, so even with repeated recrystallizations, the orange solid remained contaminated with the white LiTFMS salt.

Since metathesis displayed such poor results, we proposed to synthesize a different salt starting from the original $Rh_2(OAc)_4(MeOH)_2$. Several reagents were used including MeTFMS and HTFMS. Both of these reactions yielded red-orange solutions, but these oiled extensively and did not produce solids in any cases. This is a persistent difficulty with acidic media that generally results from water in the hygroscopic reagents. A slightly different method was successful in producing $[Rh_2(MeCN)_{10}][TFMS]_4$ from the action of Me₃SiTFMS on the tetraacetate. This is a silylating reagent as shown in the equation below:

$$\frac{\Delta}{MeCN}$$

$$Rh_{2}(OAc)_{4}(MeOH)_{2} + Me_{3}Si(TFMS) \xrightarrow{MeCN} [Rh_{2}(MeCN)_{10}][TFMS]_{4}$$
silyl esterification
$$60-70\%$$
Yield

Equation 9

This type of reagent has proven to be very effective at removing carboxylate ligands from dinuclear units, but typically the reagent is of the general form Me_3SiX for X=Cl, Br, or I.¹¹ The halide replaces the liberated anionic carboxylate to maintain the original charge on the compound. In the present case, an anion that is generally non-coordinating is used, which allows solvent to replace the transformed carboxylate. Isolation of the product was achieved in the same manner as the HBF₄ synthesis by layering hexanes and diethyl ether on the reaction solution. One difference between the two salts

was observed when the [TFMS]⁻ salt was subjected to a dynamic vacuum for several hours. The orange microcrystalline compound turned into a purple powder which redissolves in MeCN to give an orange solution. Preparing crystals of this derivative was not possible.

Spectroscopy

Substitution of trifluoromethanesulfonate for tetrafluoroborate increases the solubility of the solvated cation. $[Rh_2(MeCN)_{10}][TFMS]_4$ is soluble in acetone and alcohols, and although it appears to undergo transformations in these solvents judging by the observed color changes, the compound is sufficiently stable in these media to carry out reactions. A ¹H NMR spectrum in d⁶-acetone supports the conclusion of long term instability. If the sample is measured immediately after preparation, there is a single resonance at $\delta = 2.91$ ppm. Within 24 h, the red solution has turned olive green and gives multiple resonances at 2.95, 2.91, 2.85, and 2.76 ppm as the most prominent features. The conversion is not particularly clean, but is reproducible. Prolonged exposure to MeOH at high concentrations tends to result in precipitation of a black solid (Rh metal) from an olive-green solution

The ¹H NMR of the [TFMS]⁻ salt mimics that of the [BF₄]⁻ salt, especially with respect to its sensitivity to light. A sample recrystallized in light exhibits the same two resonances at $\delta = 2.68$ and 1.95 ppm as found for the [BF₄]⁻ compound in CD₃CN. Deuterated acetonitrile is not very diagnostic for the ligand environment due to the solvent self-exchange, so several measurements were recorded in other solvents.

The difference between the orange and purple compounds with the [TFMS]⁻ anion is easily seen in the ¹H NMR spectra recorded in CD₃NO₂. The purple species displays only one resonance at $\delta = 2.79$ ppm with no

second feature in the baseline due to axial MeCN, while the spectrum of the orange compound under the same conditions shows the axial feature at $\delta = 2.02$ ppm. The latter spectrum is shown in Figure 14. This suggests that exposure to vacuum removes the axial ligands from the $[Rh_2(MeCN)_{10}]^{4+}$ core since it is the exchange of the axial positions that produces the very broad resonance. A solution IR spectrum adds to this evidence because there are only two stretches present in the v(C=N) region of the purple compound at 2340 and 2311 cm⁻¹ while in the orange compound these two stretches are present in addition to free MeCN at 2253 cm⁻¹. The solid state infrared spectra are the most convincing, as the orange compound displays the three v(C=N) stretches typical of the decakisacetonitrile cations at 2345, 2316, and 2286 cm⁻¹ while the spectrum of the purple compound is missing the lowest energy stretch which is assigned to the axial ligands.

Molecular Structure

Selected bond distances and angles are presented in Tables 10 and 11 respectively. Positional parameters are included in the Appendix. The difference in counterion is enough to reduce the symmetry of the crystalline salt from a C-centered to a primitive monoclinic lattice. Considering the lower symmetry of [TFMS]⁻ compared to the tetrahedral [BF₄]⁻, this is not particularly surprising. The ORTEP packing diagrams of the two salts, shown in Figures 15 and 16 show the much more loosely packed lattice of the [TFMS]⁻ salt which also incorporates an interstitial solvent molecule unlike the more closely packed [BF₄]⁻ structure. The [Rh₂]⁴⁺ molecule itself, is on a general position so the entire unit is unique in the asymmetric unit in contrast to the earlier structure in which the center of the Rh-Rh bond lies on
Figure 14. ¹H NMR of the orange form of [Rh₂(MeCN)₁₀][TFMS]₄ in CD₃NO₂



Figure 14

atom	atom	distance	atom	atom	distance
RH1	RH2	2.616(2)	C11	C12	1.51(3)
RH1	N6	2.01(1)	C13	C14	1.54(2)
RH1	N7	2.00(1)	C15	C16	1.48(2)
RH1	N8	1.97(1)	C17	C18	1.51(2)
RH1	N9	2.01(1)	C19	C20	1.53(3)
RH1	N10	2.15(1)			
RH2	N1	1.97(1)			
RH2	N2	1.96(1)			
RH2	N3	1.97(1)			
RH2	N4	2.03(1)			
RH2	N5	2.14(1)			
N1	C1	1.12(2)			
N2	C3	1.13(2)			
N3	C5	1.14(2)			
N4	C7	1.06(2)			
N5	C9	1.12(3)			
N6	C11	1.10(2)			
N7	C13	1.06(2)			
N8	C15	1.15(2)			
N9	C17	1.08(2)			
N10	C19	1.15(2)			
C1	C2	1.55(2)			
C3	C4	1.51(3)			
C5	C6	1.52(3)			
C7	C8	1.48(3)			
C9	C10	1.56(3)			

Table 10. Selected Bond Distances in Å for [Rh₂(MeCN)₁₀][TFMS]₄

atom	atom	atom	angle	atom	atom	atom	angle
RH2	RH1	N6	91.3(4)	N2	RH2	N 5	91.5(6)
RH2	RH1	N7	90.4(3)	N3	RH2	N4	90.2(5)
RH2	RH1	N8	88.7(3)	N3	RH2	N 5	90.2(5)
RH2	RH1	N9	90.2(4)	N4	RH2	N 5	86.8(5)
RH2	RH1	N10	179.0(4)	RH2	Nl	C1	178(1)
N6	RH1	N7	88.3(5)	RH2	N2	C3	177(1)
N6	RH1	N8	178.6(5)	RH2	N3	C5	179(1)
N6	RH1	N9	92.7(5)	RH2	N4	С7	172(1)
N 6	RH1	N10	89.6(5)	RH2	N 5	C9	160(1)
N 7	RH1	N8	90.3(5)	RH1	N6	C11	176(1)
N7	RH1	N9	178.8(5)	RH1	N 7	C13	176(1)
N7	RH1	N10	90.2(5)	RH1	N8	C15	176(1)
N8	RH1	N9	88.7(5)	RH1	N9	C17	173(1)
N8	RH1	N10	90.5(5)	RH1	N10	C19	174(2)
N9	RH1	N10	89.2(5)	N1	C1	C2	176(2)
RH1	RH2	Nl	89.8(3)	N2	С3	C4	178(2)
RH1	RH2	N2	91.2(4)	N3	C5	C6	176(2)
RH1	RH2	N3	89.7(4)	N4	C7	C8	179(2)
RH1	RH2	N4	90.5(4)	N5	C9	C10	174(2)
RH1	RH2	N 5	177.3(4)	N6	C11	C12	180(2)
N1	RH2	N2	88.2(5)	N7	C13	C14	177(2)
N1	RH2	N3	179.5(5)	N8	C15	C16	178(1)
N1	RH2	N4	90.1(5)	N9	C17	C18	177(2)
N1	RH2	N5	90.3(5)	N10	C19	C20	178(2)
N2	RH2	N3	91.5(5)				
N2	RH2	N4	177.6(5)				

Table 11. Selected Bond Angles in Degrees for $[Rh_2(MeCN)_{10}][TFMS]_4$

Figure 15. ORTEP packing diagram of [Rh₂(MeCN)₁₀][BF₄]₄. The anions have been omitted for clarity



Figure 16. ORTEP packing diagram of [Rh₂(MeCN)₁₀][TFMS]₄. The anions have been omitted for clarity



Figure 16

a C₂ axis. With the exception of the lower crystallographic symmetry, the two $[Rh_2(MeCN)_{10}]^{4+}$ cations are virtually identical. The Rh-Rh bond of 2.617(2) is comparable to the value of 2.624(1) in the original salt. The torsion angle is slightly less than ideal at 42.8(5), but otherwise, crystal packing forces do not appear to substantially influence either the conformation or the structure of the dirhodium cation.

[Rh₂(EtCN)₁₀][BF₄]₄

Synthesis

Another strategy for increasing the solubility of the solvated dirhodium species involves the preparation of a compound with a longer alkyl chain on the nitrile. The space-filling model of $[Rh_2(MeCN)_{10}][BF_4]_4$ shown in Figure 17 shows that there is no significant steric repulsion between the staggered ligands, therefore it is possible to substitute a longer chain without disruption of the metal unit. Attempts to synthesize $[Rh_2(EtCN)_{10}][BF_4]_4$ by solvent exchange of propionitrile with the MeCN ligand did not proceed cleanly, judging by the weak v(C=N) stretches in the infrared, and by the presence of free CH_3CN in the ¹H NMR of the product. Since this route was not very productive, the best approach proved to be synthesis of the desired compound from $Rh_2(OAc)_4(MeCN)_2$. The HBF₄ method which is also the preferred synthesis for the MeCN species was employed as in the equation below:

 $Rh_{2}(OAc)_{4}(MeCN)_{2} + HBF_{4} \cdot Et_{2}O \xrightarrow{\Delta} [Rh_{2}(EtCN)_{10}][BF_{4}]_{4}$

Figure 17. Space filling model of the dimetal cation in [Rh₂(MeCN)₁₀][BF₄]₄



Figure 17

The reaction in propionitrile proceeds much faster than with acetonitrile, but work-up involves repeated iterations of crystallization due to a tendency of the solution to oil. Synthesis of the triflate salt of the propionitrile substituted cation was not successful as reactions of HTFMS or Me₃SiTFMS with $Rh_2(OAc)_4(MeCN)_2$ did not yield tractable products. The triflic acid reaction gave a red-orange colored solution, but the reaction with trimethylsilyltriflate produced a brown solution. The triflic acid is even more hygroscopic than tetrafluoroboric acid; this fact along with the increasing solubility of triflate salts probably complicates all reactions using this reagent.

Spectroscopy

The ¹H NMR of the $[Rh_2(EtCN)_{10}][BF_4]_4$ compound is more straightforward than the corresponding spectrum of the MeCN compound. Immediately after dissolution in CD₃CN, the expected 4:1 ratio of equatorial ligands to exchanged axial solvent ligands was observed; full exchange of all sites was complete within 24 hours. The FT-IR spectrum displays only two stretches in the C=N region, at 2324, and 2287 cm⁻¹ since the additional carbon removes the combination mode. The broad v(B-F) stretch occurs at 1055 cm⁻¹.

The electrochemistry of the EtCN and MeCN species are compared in Figure 18. $[Rh_2(EtCN)_{10}][BF_4]_4$ displays an irreversible reduction at $E_{p,c} =$ -0.20V vs Ag/AgCl (-.625 V vs Fc), at a slightly more negative potential than $[Rh_2(MeCN)_{10}][BF_4]_4$, and an additional second irreversible reduction at lower potential ($E_{p,c} = -0.95V$ vs Ag/AgCl, -1.375 vs Fc) that is not observed out to -2.0 V for the MeCN salt. As in the MeCN complex, the lack of an accessible oxidation is not surprising for this highly charged system. Figure 18. Cyclic voltammetry of (a) $[Rh_2(MeCN)_{10}][BF_4]_4$ and (b) $[Rh_2(EtCN)_{10}][BF_4]_4$ _





128

Molecular Structure

Tables 12 and 13 present selected bond distances and angles. Positional parameters are included in Appendix 2. An ORTEP diagram in Figure 19 depicts the dirhodium cation with only one orientation of the disordered atoms presented for clarity. In spite of the longer chain EtCN ligand, the homologous acetonitrile and propionitrile salts pack in the identical space group with the same symmetry as is effectively demonstrated in the packing diagrams depicted in Figures 15 (vide supra) and 20. The center of the Rh-Rh bond lies on a two-fold axis rendering one-half of the molecule and two of the [BF₄] ions unique. The two planes of equatorial ligands are almost perfectly staggered with respect to each other with the average N-Rh-Rh-N torsion angle equal to $44.9(2)^{\circ}$. Two equatorial ethyl groups are disordered in two orientations- C5 and C6, and C11 and C12. It is somewhat surprising that only two of the five groups displayed any significant disorder, even though multiple orientations become more likely with the increasing length of the alkyl group. The space filling diagram of the $[Rh_2(EtCN)_{10}]^{4+}$ molecule, depicted in Figure 21, shows that the longer chain nitrile does not increase the steric demands around the dimetal unit. The Rh-Rh bond of 2.6040(9) Å falls in the same range as the other crystallographically characterized nitrile salts which suggests that the Rh-Rh bond is quite robust and is not highly influenced by the identity of the ligand or crystal packing forces due to different counterions.

Other Nitriles

In an effort to test the stability limits of the Rh-Rh bond with more sterically demanding ligands, the preparation of homoleptic butyronitrile and benzonitrile complexes was attempted both by solvent exchange with the

129

atom	atom	distance	atom	atom	distance
Rhl	Rhl'	2.6040(9)	C4	C5	1.55(2)
Rhl	N1	1.991(4)	C4	C5A	1.50(2)
Rhl	N2	1.977(4)	C5	C6	1.49(2)
Rhl	N3	1.982(4)	C5A	C6A	1.53(2)
Rhl	N4	1.987(4)	C7	C8	1.456(8)
Rhl	N5	2.180(6)	C8	С9	1.528(9)
Fl	B1	1.408(8)	C10	C11	1.61(2)
F2	Bl	1.374(9)	C11	C12	1.50(3)
F3	В1	1.374(9)	C11A	C12A	1.51(2)
F4	B1	1.367(8)	C13	C14	1.54(1)
F5	B2	1.39(1)	C14	C15	1.43(1)
F6	B2	1.44(1)	C12	C12A	1.79(3)
F7	B2	1.33(1)			
F8	B2	1.31(1)			
N1	C1	1.128(7)			
N2	C4	1.122(8)			
N3	C7	1.139(7)			
N4	C10	1.101(8)			
N5	C13	1.148(9)			
C1	C2	1.460(8)			
C2	C3	1.54(1)			

Table 12.	Selected	Bond	Distances	in 4	Å for	[Rh ₂ (EtCN)	10][BF4]4

atom	atom	atom	angle	atom	atom	atom	angle
Rhl	Rhl'	N 1	91.2(1)	C4	C5	C6	107(2)
Rh1	Rhl'	N2	91.0(1)	C4	C5A	C6A	103(1)
Rhl	Rhl'	NJ	88.6(1)	N3	C7	C8	178.1(6)
Rhl	Rhl'	N4	91.6(2)	C7	C8	C9	111.8(5)
Rhl	Rhl'	N5	176.9(2)	N4	C10	C11	165(1)
Nl	Rhl	N2	91.3(2)	N4	C10	C11A	161(1)
Nl	Rhl	N 3	179.0(2)	C10	C11	C12	101(2)
N1	Rhl	N4	89.1(2)	C10	C11A	C12A	96(2)
N1	Rhl	N 5	87.1(2)	N5	C13	C14	177.7(9)
N2	Rhl	N 3	89.8(2)	C13	C14	C15	108.4(8)
N2	Rhl	N4	177.4(2)				
N2	Rhl	N 5	86.4(2)				
N3	Rhl	N4	89.9(2)				
N 3	Rhl	N5	93.1(2)				
N4	Rhl	N 5	91.1(2)				
Rhl	Nl	Cl	171.9(4)				
Rhl	N2	C4	170.6(6)				
Rhl	N 3	C7	178.0(4)				
Rhl	N4	C10	175.2(7)				
Rhl	N5	C13	157.4(6)				
N 1	C1	C2	178.5(6)				
C1	C2	С3	112.5(6)				
N2	C4	C5	166(1)				
N2	C4	C5A	165(1)				
C5	C4	C5A	28.8(7)				

Table 13. Selected Bond Angles in degrees for [Rh₂(EtCN)₁₀][BF₄]₄

Figure 19. ORTEP diagram of the dimetal cation in $[Rh_2(EtCN)_{10}][BF_4]_4$



Figure 20. ORTEP packing diagram of [Rh₂(EtCN)₁₀][BF₄]₄. The counterions have been omitted for clarity



Figure 20

Figure 21. Space filling diagram of the cationic component of [Rh₂(EtCN)₁₀][BF₄]₄



Figure 21

MeCN and EtCN species, and by synthesis from $Rh_2(OAc)_4(MeCN)_2$, but solids were not isolated. This is largely due to the increased solubility of these species as well as the typical problems with the acidic medium, although the use of Et₃OBF₄ was not any more successful than HBF₄. Synthesis of a butyronitrile complex does appear to proceed from the action of HBF₄ on $Rh_2(OAc)_4(MeCN)_2$, judging from the orange color of the reaction solution, but no solid was obtained. The chemistry of $Rh_2(OAc)_4(MeCN)_2$ and HBF₄ with benzonitrile produces a brown intractable solution. Solvent exchange with the acetonitrile salt is not clean, but dissolving the propionitrile salt in benzonitrile produces an orange solution similar to those of the other nitrile salts. The extreme solubility of the product has thus far prevented isolation of the compound, but it appears that $[Rh_2(EtCN)_{10}][BF_4]_4$ may be a useful route to compounds that are inaccessible from the MeCN analog.

Substitution reactions were also carried out with bidentate nitriles. We proposed that if monodentate nitriles adopt a perfectly staggered disposition across the M-M bond, perhaps the unit could be forced into an eclipsed mode by tethering together two of the ligands. Pentanedinitrile, or glutaronitrile, is exactly that- two acetonitrile ligands are tied together by a methylene bridge. Figure 22 depicts the ligands and the proposed products of these with the $[Rh_2]^{4+}$ unit. It is important to pursue the X-ray structures of these compounds, as determining the Rh-Rh bond length crystallographically would afford the first opportunity to compare the metal-metal distances of bridged and unbridged metal systems with similar ligand sets. The neutral σ -donors such as MeCN cannot be validly compared with anionic π -donors like carboxylates. Figure 22. Diagram of the postulated staggered vs. eclipsed conformational differences with monodentate and bidentate nitriles







Pentanedinitrile

On initial examination, it appears that bridging a dimetal unit by pentanedinitrile is very unlikely due to the necessity of forming a ninemembered ring. This is actually not quite the case since the C-C=N unit is relatively rigid so flexibility at each atom will not be observed. Propanedinitrile (malononitrile) was also investigated, but there is less flexibility in this ligand due to the presence of only one sp³ hybridized carbon; furthermore, the bite size may be too large for this dimetal unit.

Our main interest in these complexes, is that bidentate nitriles should help to stabilize the Rh-Rh bond in substitution reactions that led to metalmetal bond cleavage. The bridging nitrile ligands should not alter the electronic structure of the molecule substantially, but may change the environment sufficiently to allow more reactive species to be stabilized.

Bifunctionalized nitriles have been previously used as ligands that either bridge or coordinate monofunctionally.¹² In the present case of homoleptic nitrile systems, there is good potential for polymeric networks to be established through two units sharing an axial ligand. To encourage the isolation of discrete molecules, acetonitrile was added upon work-up in an attempt to substitute the axial positions and thereby break up any existing networks.

Unfortunately in our synthetic work, substitution for bidentate nitriles has encountered many of the same problems as with the longer monofunctionalized nitriles. Solvent exchange is incomplete with the starting material, $[Rh_2(MeCN)_{10}][BF_4]_4$, and isolation from acidic media was not possible. Additional problems were encountered when the reactions were carried out in neat dinitrile, as this liquid displays limited miscibility with other organic solvents which further restricts options for subsequent work-

up.

141

Carboxylate Reactions

Our efforts to determine the stability of the metal-metal bond in $[Rh_2(MeCN)_{10}]^{4+}$ were not limited to substitution of MeCN for other nitrile ligands. Elementary reactivity studies were performed with a variety of different donors to elucidate the ability of this starting material to be used in designed synthesis. The most obvious starting point was to attempt to convert the complex back to $Rh_2(OAc)_4(MeOH)_2$. This reaction is quite straight forward; indeed reaction of $[Rh_2(MeCN)_{10}]^{4+}$ with acetic acid and sodium acetate leads to a green solid that after recrystallization from MeOH, was verified as dirhodium tetraacetate.

During the course of our studies, Chisholm and coworkers reported the findings on the lability of dirhodium and dimolybdenum carboxylate complexes, which they supported with a theoretical argument.¹³ They found that the equatorial MeCN ligands in $[Rh_2(OAc)_2(MeCN)_6]^{2+}$ were not substitutionally labile unlike the Mo analog.^{13,14} It was of interest to their studies as well as ours to ascertain the lability of the equatorial MeCN groups in $[Rh_2(MeCN)_{10}]^{4+}$, especially with respect to replacement with carboxylate ligands. While carboxylate removal in going from $Rh_2(OAc)_4(MeCN)_2$ to $[Rh_2(MeCN)_{10}]^{4+}$ appears to occur with cis geometry to give the intermediate cis- $[Rh_2(OAc)_2(MeCN)_6]^{2+}$, this may be a kinetic rather than thermodynamic product. Trans carboxylates are not out of the question in reactions of the cis-carboxylate compounds as seen in the cis to trans isomerization in the reaction of $[Mo_2(OAc)_2(MeCN)_6]^{2+}$ and dmpe.¹⁵

Many attempts were made to prepare a bis-carboxylate product from the $[Rh_2(MeCN)_{10}]^{4+}$ in order to observe its disposition of carboxylate ligands. Reactions with sodium acetate and its hydrate are hampered by their low solubility, and more soluble carboxylates such as sodium butyrate and sodium trifluoroacetate led to brown solutions. In one reaction with sodium acetate, a purple solution resulted that gave electronic spectra similar to that of cis- $[Rh_2(OAc)_2(MeCN)_6]^{2+}$, but considering both the irreproducibility of this result as well as the diagnosed impurity of the starting material we strongly suspect that the product was merely an impurity in the solvated compound.

One unusual result emerged from the reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with Na[O₂C₄H₇]. Two equivalents were added originally, and due to a persistent lack of solubility in MeCN, slightly more than two more equivalents were added to favor the forward reaction. The solution turned purple and was then pumped to a solid. The solid turned green after prolonged vacuum. A ¹H NMR spectrum revealed that this produce was $Rh_2(O_2C_4H_7)_4$, signifying that the reaction had gone beyond the desired biscarboxylate stage.

Axial Substitution

In spite of its relative insolubility in most common solvents, $[Rh_2(MeCN)_{10}]^{4+}$ undergoes axial exchange reactions in various media. The most marked example is axial solvent exchange in the solid state. Upon addition of a small volume of MeOH, THF, or acetone to a sample of the $[BF_4]^{\cdot}$ salt, the color was seen to change without dissolution of the compound. In MeOH, the solid turns red, in THF- pale orange, and in acetone- olive green. Figure 23 shows the v(C=N) region in the infrared spectra of the new solids. With the exception of the axial MeCN spectrum which is presented for comparison, each spectrum shows loss of the axial MeCN stretch. Features of the incoming axial donor may also be observed in each spectrum. Figure 23. Comparison of the infrared spectra of the axial solvent substitution with $[Rh_2(MeCN)_{10}][BF_4]_4$

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Solvent Exchange, Rh₂(aq)⁴⁺

Synthesis

Solvent exchange is of course more facile when the salt is soluble in the new medium. It occurred to us that $[Rh_2(MeCN)_{10}]^{4+}$ was an excellent entry point into Taube's aquarhodium species in the absence of acid. $[Rh_2(MeCN)_{10}][BF_4]_4$ is completely soluble in water and turns red upon initial dissolution. After refluxing, the solution converts to a purple color; subsequent periodic pumping to remove the liberated MeCN results in further color changes to blue, and finally green. These color changes are typical of the substitution of nitrogen donors for oxygen donors. The reaction to produce the MeCN solvate proceeds in exactly the opposite order; the green compound, $Rh_2(OAc)_4(MeOH)_2$, turns purple when dissolved in MeCN as the axial positions exchange oxygen-donor MeOH for MeCN, and goes through red to orange as the ligand environment becomes rich in nitrogen donors. One advantage of our method to access an agua compound that differs from Taube's is that we use water as opposed to acid, therefore our solvent may be removed *in vacuo* to yield a green solid. We attempted to crystallize the aqua compound by eluting it with strong acid from a Dowex cation exchange column. The compound was eluted anaerobically with 4 \underline{M} ptoluenesulfonic acid, and the resulting solution was purged with N_2 to encourage evaporation. No crystals have been obtained to date, but the method appears to be very promising.

Spectroscopy

Since crystallization of aqua species is difficult, more practical methods of characterization and comparison were employed. Table 14 compiles the values obtained for the electronic spectrum of our product along with those

146

Table 14. Summary of Spectral and Reactivity Properties for $Rh_2(aq)^{4+}$

	Synthesized from [Rh ₂ (MeCN) ₁₀] ⁴⁺	Synthesized from [Rh(H ₂ O) ₅ Cl] ²⁺ and Cr ²⁺
λ max in H ₂ O	587 nm	a
$\lambda \max \text{ in } 3\underline{M} \text{ HClO}_4$	600 nm b 580 nm c	648 or 630 nm
converts back to Rh2(OAc)4 in CH3COOH	yes	yes

- a value was not reported in H_2O as the sample can not be isolated from (a) $3 \underline{M} HClO_4$
- (b)
- sample was prepared in H_2O sample was prepared in 3 <u>M</u> HClO₄ (c)

reported by Taube.¹⁶ Since Taube's group was unable to separate the compound from the acid, there is no report of a spectrum of that species in water; Instead their data were reported in $3 M HClO_4$. In order to make a valid comparison of our work to theirs, we also collected data in 3 M HClO₄. A λ_{max} value of 600 nm was observed for the complex prepared in water and redissolved in acid before the spectrum was taken. This was quite reproducible, and is most likely of a pure compound because the sample was anaerobically eluted off a cation exchange column prior to spectroscopic characterization. The second value was obtained from the compound isolated from the synthesis of the aqua species from $[Rh_2(MeCN)_{10}][BF_4]_4$ in acid. We attribute the slight variations in the values among all methods of preparation to the different pH values for each preparation. Varying degrees of hydrolysis of the H_2O ligands would alter the structure and therefore affect the electronic spectrum of the compound. Taube verified that the Rh_2^{4+} core was intact in his $Rh_2(aq)^{4+}$ compound by its ease of conversion back to $Rh_2(OAc)_4$. The same procedure was repeated with our green solid with identical results.

The infrared spectrum of the sample of "Rh₂(aq)⁴⁺" prepared in this study displays both stretches and bends due to the presence of water; these are 3449, 3356, 1657, 1601, and a large feature due to [BF₄]⁻ at 1070 cm⁻¹. There was no evidence for MeCN apparent in the spectrum. A cyclic voltammogram in 0.1 <u>M</u> KBF₄ in water displayed a single quasi-reversible reduction at $E_{1/2} = 0.29V$. The ¹H NMR spectrum in CD₃CN has three significant resonances, one at $\delta = 1.87$ ppm (s,), a doublet at $\delta = 1.78$ ppm, and a third feature at $\delta = 1.69$ ppm. The spectrum in D₂O is slightly different with four singlet resonances at $\delta = 1.82$, 1.79, 1.74 and 1.68 ppm in approximately a 5:2:4:4 ratio. The ¹H NMR spectrum of $[Rh_2(MeCN)_{10}][BF_4]_4$ dissolved in D₂O displays several singlet resonances close together at $\delta = 2.47, 2.45, 2.43$, and 2.42 ppm as well as a doublet at 1.93 and a large singlet at 1.87 ppm. These features are attributed to a combination of free solvent and coordinated solvent in several different environments.

Interconversions of the Rh₂⁴⁺ core

Figure 24 summarizes the variety of interconversions we have found possible for the $[Rh_2]^{4+}$ compounds in this study. The tetraacetate may be used to synthesize the decakisacetonitrile compound from which the water compound may be prepared, and from there, conversion back to the acetate is quite facile. The reverse reactions are not as accessible. The decakisacetonitrile species can be converted back to dirhodium tetraacetate, but whether or not the water compound may be accessed from there is questionable. As mentioned in the Introduction of this dissertation, Wilkinson and coworkers had reported that it is possible,¹⁷ but Taube's group challenged these findings.¹⁸ Certainly our success with acidic syntheses in our research prove that it is possible to remove all the carboxylates from $Rh_2(OAc)_4$ by this method. The final exchange of acetonitrile for water does not proceed to completion. This is not surprising for several reasons. Firstly, the pH of the reaction solution is quite low, suggesting that the rhodium compound has undergone considerable hydrolysis. If this is the case, OH⁻ ligands as well as H_2O ligands are present in the coordination sphere, and it is highly unlikely that neutral acetonitrile groups will replace anionic hydroxides. Secondly, the forward reaction is driven by periodic pumping to remove the liberated MeCN ligands. This is possible because acetonitrile has a lower boiling point than water. In the reverse direction, this situation

Figure 24. Interconversions of the [Rh₂]⁴⁺ core

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Figure 24

prevents the free water from being removed from the system thus setting up an equilibrium between the two fully solvated species.

Pyridinc and Bipyridine Reactions

Efforts to prepare a $[Rh_2(py)_{10}]^{4+}$ such as simple solvent exchange have not met with substantial success. $[Rh_2(MeCN)_{10}][BF_4]_4$ is not soluble in pyridine even with gentle warming. Other attempts to prepare the complex from $Rh_2(OAc)_4(MeOH)_2$ led to a pink insoluble polymer, and yellow crystals whose color suggests a Rh(III) mononuclear species.¹ Two X-ray structures were carried out on these crystals, but due to severe twinning problems, the structures were never solved.

In the case of the 2,2'-bipyridine chemistry, the best solvent proved to be CH_3NO_2 which neither degrades the starting material as acetone does, nor competes strongly for the coordination sites as does MeCN. Reaction in this medium of 4 equivalents of bpy with $[Rh_2(MeCN)_{10}][BF_4]_4$ produced a green compound with an unusual ¹H NMR spectrum. The resonances in the bpy region are shifted with respect to the free ligand as expected for coordinated bpy, but the sets of bpy protons fall at different chemical shifts with respect to one another than in most dinuclear bpy complexes.¹⁹ Perfection of the synthesis and isolation of this product is extremely desirable so that X-ray quality crystals may be grown of the pure compound.

Reaction with 2 equivalents of bpy also yields a product with a similar pattern in the ¹H NMR spectrum, but appearing at different chemical shifts than the 4 bpy reaction, although we are aware that the difference in deuterated solvent makes comparison a bit less valid. Further study of this system is in progress.

Tertiary Phosphine Reactions

Reactions between tertiary phosphine ligands and the $[Rh_2(MeCN)_{10}]^{4+}$ complex pairs two relatively incompatible types of systems. The highly charged dirhodium unit is a hard acid whereas the phosphines are softer bases. The inability of these two to form a stable complex is evidenced by the reaction solution initially turning red, but quickly reverting back to the orange color of the pure starting material upon work-up. This result was the same for monodentate (PMe₃) or bidentate (dppm) phosphine ligands. Orange solids isolated from these reactions displayed ¹H NMR spectra typical of the original fully solvated tetracation.

The one phosphine that readily produces a new complex is the highly basic and bulky functionalized phosphine, TMPP, mentioned in the introduction of this Chapter. This ligand apparently binds so strongly in the axial position that the M-M bond is disrupted, and the bulk of the pendant groups prevents reformation of the dinuclear unit.² In the absence of bulk and pendant groups, phosphines evidently do not compete effectively for coordination sites occupied by the solvent, so there is no net reaction. This was also confirmed independently by Baranovskii and coworkers in their study of PPh3 with $[Rh_2(MeCN)_8(H_2O)_2]^{4+.20}$

Chloride Reactions

It was anticipated that the cation would readily bind the anionic halides easily to balance the charge, but the reactions carried out with chloride donors have produced inconclusive results. Further work is necessary to elucidate this chemistry.

153

Oxygen Reactions

It is apparent that oxygen reacts with the $[Rh_2(MeCN)_{10}]^{4+}$ only in the presence of light. In the absence of photochemical conditions, the reaction of MeCN solutions of the complex with O₂ produce only the pure compound as verified by a unit cell of a crystal grown in the dark from one of these reaction solutions. A further discussion of the photochemistry of this compound is found in Chapter IV of this dissertation.

E. Summary

Several different forms of homoleptic nitrile dirhodium species were prepared that possess subtle differences in their reactivity. $[Rh_2(MeCN)_{10}][BF_4]_4$ is the least soluble of the three, and exhibits extensive photochemistry, detailed in Chapter IV of this dissertation. $[Rh_2(MeCN)_{10}][TFMS]_4$ crystallizes in a loosely packed lattice that facilitates removal of the axial groups in the solid state. The salt, $[Rh_2(EtCN)_{10}][BF_4]_4$, is the most stable of the group and the most readily prepared. Preliminary results of the chemistry of $[Rh_2(EtCN)_{10}]^{4+}$ indicates that it does not undergo the same photochemistry as the acetonitrile complex. Solvent exchange occurs readily with $[Rh_2(EtCN)_{10}]^{4+}$, although the $Rh_2(aq)^{4+}$ species is conveniently prepared from the $[Rh_2(MeCN)_{10}][BF_4]_4$

The fundamental reactivity of these species was broadly explored. Reactions with bidentate anions with the exception of acetate has not been investigated since these ligands will not test the subtle changes induced by substitution of neutral acetonitrile donors for other neutral donors. Phosphine ligands are generally incompatible with this hard acid, and the results with chlorides are not conclusive. The reactions of two and four equivalents of bipyridine are quite interesting, and underscore the compatibility of the $[Rh_2]^{4+}$ core for neutral nitrogen donor ligands. These substitution reactions occur much more cleanly in a non-nitrile medium. Further study of these reactions would be particularly interesting.

A very useful tool in much of this chemistry would be the application of ¹⁰³Rh NMR. As the products become less symmetrical in their electron distribution due to mixed-donor ligand sets, the possibility for observing a ¹⁰³Rh signal increases. This method could be extremely helpful in indicating oxidation state and coordination environment in systems for which the ¹H NMR spectrum shows only exchanged solvent. Future directions of this research will make use of this metal NMR tool.

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CHAPTER IV

PHOTOCHEMISTRY OF [Rh₂(MeCN)₁₀][BF₄]₄

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A. Introduction

In an effort to further elucidate the properties of the solvated dinuclear rhodium compound, $[Rh_2(MeCN)_{10}][BF_4]_4$, we collaborated with scientists at Los Alamos National Laboratories to examine the Raman stretching frequency of the Rh-Rh single bond. During the Raman experiment, the spectrum bleached, indicating that the compound had decomposed. Later, a reexamination of the sample revealed that the original electronic spectrum had been reestablished. Subsequent experiments proved that this compound undergoes reversible photochemistry on the kilosecond time scale. We proposed to further study the synthetic aspects of this chemistry to further elucidate the photochemical process.

B. Experimental, Synthesis

(1) Thermal Decomposition of $[Rh_2(MeCN)_{10}][BF_4]_4$ in Solution

A quantity of 2 (33.7 mg, 0.035 mmol) was dissolved in 3 mL of a 1:1 solution of MeCN : tetraglyme. The solution was wrapped in foil and refluxed. The Rh starting material was not completely soluble, therefore the solution was decanted, and 10 mL of MeCN was added to the solution. The solution was refluxed overnight after which the solution was immediately decanted into a quartz UV-visible cell for further examination. Spectra were recorded at frequent intervals as the solution cooled.

(2) Reduction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with the Tris(2,6dimethoxyphenyl) Methyl Radical

Two solutions were prepared for this experiment. In the first, 80 mg (0.083 mmol) of 2 and 450 mg (1.37 mmol) of TBABF₄ were stirred in 10 mL of MeCN until everything had dissolved. The second solution contained 77

159

mg of tris(2,6-dimethoxyphenyl) methyl radical (0.083 mmol, 1.0 equiv.) in 20 mL of MeCN. The solution containing the radical was added to the metal solution, with the appearance of the dark purple of the organic cation masking any new compounds. Approximately 2 g of TBABF4 was added to the solution to encourage precipitation of a gray solid which was collected by filtration in air. A Nujol mull IR spectrum did not reveal any characteristic features other than the $[BF4]^-$ anion at 1070 cm⁻¹. The solid was collected on a frit and washed with CH₂Cl₂ until the washings were clear (5 x 10 mL). A small amount of the solid dissolved in 2 mL of MeCN to give an orange solution. At time intervals of approximately 5-10 min., the solid was again washed with CH₂Cl₂, and each time the washings began as a purple color and were continued until the solutions were colorless.

(3) Reduction of $[Rh_2(MeCN)_{10}]^{4+}$ with Na-Acenaphthylenide (NaAce)

Quantities of 2 (104 mg, 0.108 mmol) and 632.6 mg $[n-Bu_4N][BF_4]$ (1.921 mmol) were dissolved in MeCN after which the solution was wrapped in foil and chilled in a MeCN/CO₂ bath to -42°C. To this solution was slowly added 10.8 mL of recrystallized NaAce (0.010 M in THF) and THF (10 mL) which were also chilled to -42 °C. The solution was then allowed to settle revealing a yellow solution and a dark brown solid which was filtered to collect the solid. The yellow solution, with the characteristic color of acenaphthylene and containing excess [n-Bu₄N][BF₄] was discarded. The brown solid was washed with diethyl ether (3 x 10 mL) and dried *in vacuo*. Yield 91 mg, (94% yield based on a theoretical yield of 86 mg of [Rh₄(MeCN)₁₆][BF₄]₆ and an additional 11 mg of NaBF₄). ¹H NMR (CD₃CN), ppm: $\delta = +1.95$ (free CH₃CN). IR(KBr, Nujol), cm⁻¹: 2337 (s), 2316 (m), 2281 (m), 1070 (s, br). UV-visible (MeCN, anaerobic, nm (ϵ in M⁻¹ cm⁻¹)) 425 (1080), 305 (20,200).

(4) Reduction of [Rh₂(MeCN)₁₀][BF₄]₄ with Cobaltocene

A quantity of 2 (49.9 mg, 0.052 mmol) was added to solid cobaltocene (9.9 mg, 0.052 mmol, 1.0 equiv.) in a Schlenk tube. Without addition of solvent, the mixture of solids turned black within ten minutes. Acetone was added which gradually dissolved the solids, but no product was ever isolated.

(5) Reduction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with Cobaltocene in the presence of Electrolyte

An amount of 2 (95 mg, 0.99 mmol) was dissolved in 5 mL of MeCN together with 200 mg of NaBF₄ (1.822 mmol). To this solution was added a solution of CoCp₂ (19 mg, 0.100 mmol, 1.0 equiv.) and 463 mg of [*n*-Bu₄N][BF₄] (1.406 mmol) dissolved in 5 mL of acetone. The two solutions instantly produced a dark green solid suspended in a red-brown solution. The solution was filtered and the solid was dried under vacuum; yield, 263 mg. UV-visible spectrum of the solid redissolved anaerobically in MeCN, $\lambda_{max} = 414$ nm, shoulder at ~470 nm.

(6) Crystallization Attempt of the Cobaltocene Reduction Product

Two solutions were prepared, one containing 102.5 mg of 2 (0.106 mmol) and 210 mg of NaBF₄ in 5 mL of MeCN, and a second solution of 20 mg of CoCp₂ (0.106 mmol, 1.0 equiv.) and 464 mg of TBABF₄ in 5 mL of 1:1 toluene : acetone. The flasks containing these solutions were wrapped in foil. The first solution was layered on the second solution by cannula transfer. A black-green powder immediately appeared at the solution interface, but the

layers did not mix further at this time. Over ten days, needle-like microcrystals began growing from the interface into the upper layer. Diffusion was complete two days later, yielding a large amount of fluffy green precipitate and a yellow solution. When the solution was filtered, the mass of solid at the bottom proved to contain a large amount of red-orange crystals of the starting material and only microcrystals of the green product. An EPR carried out on a solid isolated in air displayed a very broad signal suggesting that the compound was paramagnetic, although this may have been caused by exposure to air which occurred during sample preparation. A ¹H NMR displayed principally free CH₃CN (δ = +1.95 ppm, s) and a small amount of butylammonium contamination, (3.05, (m), 1.58 (p), 1.33 (sextet), 0.96 (t)).

(7) Reduction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with NaEt₃BH

A sample of 2 (56 mg, 0.058 mmol) and 663 mg of TBABF₄ (2.021 mmol) were stirred together and warmed gently in 10 mL of MeCN until they dissolved. To this was added 0.058 mL of NaEt₃BH (0.058 mmol, 1.0 equiv.). A flocculent brown precipitate and a red solution immediately resulted. The solution was filtered by cannula and the solid was collected, washed with diethyl ether (2 x 5 mL), and dried *in vacuo*. A solid state EPR sample was prepared anaerobically and displayed no signal. The brown solid was not particularly soluble in MeCN, so a ¹H NMR measurement was not possible. IR(CsI, Nujol), cm⁻¹: 2361(m), 2339 (m), 1051 (s), 1020 (s).

(8) Bulk Electrochemical Synthesis of "[Rh4(MeCN)₁₆][BF4]6"

A sample of 2 (60 mg, 0.062 mmol) was dissolved in a .2 <u>M</u> solution of TBABF₄ in MeCN (~ 10 mL) and placed in a four compartment electrochemical cell with coarse frits separating each compartment. After a

clean blank was established, the potential was set to -0.50V and the sample was electrolyzed for 45 minutes. The solution was filtered in air and pumped to dryness. Solids from this reaction displayed a simple EPR signal, at g = 2.158

(9) Electrocrystallization of [Rh₄(MeCN)₁₆][BF₄]₆

A volume of MeCN (20 mL) was used to dissolve a sample of $[Rh_2(MeCN)_{10}][BF_4]_4$ (103 mg, 5 x 10⁻³M) and 1.323 g TBABF₄ (0.2 M solution). This solution was placed in both sides of an electrochemical cell designed for electrocrystallization (see Figure 25). The experiment was carried out at a constant current of $10 \ \mu A$ with two Pt wire electrodes. No reaction was observed to occur initially, therefore the solution was removed from the cell and 5.292 g of TBABF₄ was added to bring the total concentration up to 1 M. The solution volume was reduced to ca. 8 mL, and then returned to the cell. Additional MeCN solvent was added until the solution level was just above the level of the Pt wires (~ 2 mL). A small quantity of $[Rh_2(MeCN)_{10}]^{4+}$ precipitated due to the extreme salt concentrations, so the cell was warmed in an attempt to resolve this problem. Crystals grew at the electrode in the form of tiny needles in several days. Electrolysis continued for four more days until the current setting was increased above $30 \ \mu A$ at which point all the solid dissolved to form one chamber of dark green solution that did not diffuse through the frits. In a separate attempt, the electrode with the attached crystals was removed to view the crystals under the microscope. The very sensitive and hygroscopic crystals quickly turned into an oily residue after exposure to air and the heat of the microscope lamp.

Figure 25. Diagram of a three compartment electrocrystallization cell

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Figure 25

(10) Reaction of $[RhCl(COD)]_2$ with TlPF₆

A sample of [RhCl(COD)]₂ (200 mg, 0.406 mmol) was reacted with TlPF₆ (300 mg, 0.859 mmol, 2.12 equiv.)) in 5 mL of MeCN under mild heating conditions. The orange solid immediately dissolved to form a golden yellow solution which produced a large amount of pale yellow precipitate. The solution was decanted and reduced to a residue after efforts to cause precipitation by addition of CH₂Cl₂ failed. Yield of the white TlCl was 170 mg, (0.709 mmol, 1.75 equiv.). ¹H NMR of the residue from the yellow solution supported the conclusion that both chlorides were removed and both COD ligands were bound. (CD₃CN), ppm: $\delta = 4.47$ (m, 2 H), 2.42 (m, 2H), 1.95 (s, free CH₃CN). Further refluxing in MeCN/toluene solution for 1 week did not alter the composition of the solid.

(11) Reaction of RhCl₃ with TlPF₆

A quantity of $RhCl_3 \cdot 3H_2O$ (100 mg, 0.380 mmol) and $TlPF_6$ (500 mg, 1.43 mmol, 3.76 mmol) was refluxed in 8 mL of MeCN for 24 h. The $RhCl_3$ was not in a soluble form, so it merely turned lighter as the particle size was reduced by stirring. The solution was pumped to dryness, after washing the residue with MeCN, a pale yellow solution ensued even though the solid did not dissolve significantly.

When the same reaction was carried out by first dissolving the RhCl₃ in MeOH, reducing it to a residue under vacuum, and then adding the MeCN and the TlPF₆, a yellow solution and a white solid resulted. The yellow solution was decanted from the AgCl and layered with 15 mL of diethyl ether to obtain a bright yellow precipitate which was washed with diethyl ether and dried *in vacuo*; yield, 233 mg, (2.56 equiv.) ¹H NMR (CD₃CN, dilute), ppm: $\delta = 1.95$ (free CH₃CN). UV-visible ($\lambda_{max} = 382$ nm, shoulder at 303 nm). IR(CsI, Nujol), cm⁻¹: 2347 (vs), 2317 (m), 1292 (m), 1128 (m), 1039 (m), 835 (vs), 559 (s), 470 (s), 364 (m), 270 (w).

(12) Reaction of RhCl₃ with SbCl₅

A sample of RhCl₃ · $3H_2O$ (206 mg, 0.078 mmol) was refluxed in 8 mL of MeCN overnight. To this solution was added 812 mg SbCl₅ · 1.14 MeCN (0.235 mmol, 3.01 equiv.) dissolved in 5 mL of MeCN. The mixture was refluxed for 4 days, after which the tan-orange solution was cooled to yield a small crop of crystals and a small amount of brown residue was removed by cannula. The resulting solution was reduced to a low volume to precipitate a bright yellow solid. The solid dissolves in CH₂Cl₂, and turns brown in contact with diethyl ether. The yellow product was redissolved in MeCN, and toluene was layered under this solution to produce X-ray quality crystals. ¹H NMR (CD₃CN), ppm: $\delta = 2.62$ (s, 12 H, coordinated CH₃CN), 1.95 (s, 1 H, free CH₃CN)

(13) Reaction of RhCl₃ with AgBF₄

RhCl₃ · 3H₂O (101.4 mg, 0.385 mmol) and AgBF₄ (247 mg, 1.27 mmol, 3.30 equiv.) were stirred at r. t. in 8 mL of MeCN for three weeks. The initially insoluble reactants eventually dissolved to yield a bright yellow solution over a dingy white solid. The white solid was carefully removed by cannula. Addition of 15 mL of diethyl ether and chilling the solution to -40 °C led to precipitation of more white solid and orange crystals. UV-visible (MeCN): $\lambda_{max} = 372$ nm, shoulder at 304 nm. IR(CsI, Nujol), cm⁻¹: 2349 (m), 2314 (m), 2284 (m), 1716 (w), 1020 (s, br), 375 (w).

(14) Reaction of RhCl₃ with AgTFMS

A sample of RhCl₃ hydrate (200 mg, 0.760 mmol) was stirred in 5 mL of MeOH until it dissolved, at which point the solution was pumped to a residue. The residue was redissolved in 8 mL of MeCN and transferred under N_2 into a vessel containing 585 mg of AgTFMS (2.277 mmol, 3.0 equiv.). This solution was refluxed for five hours, after which the yellow solution was decanted from a white solid (AgCl) and chilled at -20 °C to induce precipitation. The product was not extremely soluble in MeCN as evidenced by the layer of yellow crystals that were admixed with the AgCl after the solution had been decanted. MeCN was added to the solids and the solution was warmed gently to dissolve the product. Upon cooling, a fine yellow powder precipitated. Both the original reaction solution and the MeCN washings of the white product produced yellow solids that were invariably contaminated by AgCl which we found could not be completely separated from the desired product. When the combined products were isolated in the solid state, decomposition occurred within several days upon exposure to light, regardless of aerobic or anaerobic storage, evidenced by a dark gray color of the original yellow solid. This implies that the light sensitive Ag⁺ was present in significant quantities. UV-visible ($\lambda_{max} = 412$ nm). ¹H NMR (CD₃CN): $\delta = 2.62$ (s, low intensity, coordinated CH₃CN), 1.95 ppm (s, free CH₃CN). IR(CsI, Nujol), cm⁻¹: 2351 (s), 2323 (m), 1280 (s), 1224(s), 1154 (s), 1034 (s), 752 (w), 639 (s), 569 (w), 520 (w), 463 (w), 362 (s).

(15) Synthesis of [RhCl₂(MeCN)₄][BF₄]

An amount of $RhCl_3 \cdot 3H_2O$ (203 mg, 0.771 mmol) was dissolved at r. t. in 5 mL of freshly distilled MeOH. After the solid had dissolved (~ 5 min.), the solution was reduced to a residue under vacuum. The sticky solid was

168

redissolved in 5 mL of MeCN, and the resulting solution was transferred under N₂ into 0.7 mL of HBF₄/diethyl ether solution and refluxed without stirring for 1 day. After this, some product had already precipitated. When the solution cooled, it was layered with 1 mL of hexanes and 10 mL of diethyl ether to induce additional precipitation. The solid was recrystallized from large amounts of MeCN; combined yield, 235 mg (72%). Anal. Calcd for $C_8H_{12}BCl_2F_4N_4Rh$: H, 2.84; C, 22.62; N, 13.2. Found: H, 2.77; C, 22.93; N, 12.82. ¹H NMR (CD₃CN) ppm: $\delta = 2.62$ (s, coordinated CH₃CN), 1.95 (s, free CH₃CN). IR(CsI, Nujol), cm⁻¹: 2355 (vs), 2322 (m), 1101 (vs), 1064 (vs), 1026 (vs), 960 (m), 517 (w), 469 (m), 451 (w), 360 (s), 270 (w). UV-visible (MeCN, nm (ϵ in <u>M</u>⁻¹ cm⁻¹), 414 (130), 235 (32,000), shoulder at 300 nm.

(16) Synthesis of [RhCl₂(MeCN)₄][TFMS]

An amount of RhCl₃·3H₂O (208 mg, 0.790 mmol) was stirred in 5 mL of MeOH for 5 min. until the solid had dissolved to form a red solution. This was reduced to a residue under vacuum and redissolved in 5 mL of MeCN, after which HTFMS (0.5 mL) was added anaerobically, and the reaction was refluxed for 4 h. Cooling the solution resulted in the deposition of a yellow solid on the bottom of the reaction vessel. The volume was reduced slightly and then 5 mL of 1:1 CH₂Cl₂ : diethyl ether was added to precipitate large amounts of the yellow solid. The product was washed with toluene and pumped to dryness; yield, 360 mg (94%). ¹H NMR (CD₃CN), ppm: $\delta = 2.62$ (s, coordinated CH₃CN), 1.95 (s, free CH₃CN).

(17) Reaction of [RhCl₂(MeCN)₄][BF₄] with [Na]⁺[mhp]⁻

Two solutions were prepared, one containing 50 mg of unrecrystallized [RhCl₂(MeCN)₄][BF₄] (0.190 mmol) in 5 mL of MeCN, and one containing 13

mg of NaOMe (0.241 mmol) and 51 mg of Hhmp (6-methylhydroxypyridine, 0.467 mmol) in 5 mL of MeOH. The rhodium starting material was evidently not pure as we observed some white solid that was insoluble in MeCN. The solution was filtered before use, but the stoichiometry of the reaction was altered by this impurity. The solution of [Na][mhp] was transferred anaerobically to the filtered Rh solution which first turned a gold-yellow color and then changed to a pale olive green in 24 h. Reduction of the volume caused the precipitation of a pale gray solid and layering of diethyl ether (~ 8 mL) produced more solid. The solution was decanted and layered with toluene to produce additional dirty white solid. No colored products were isolated.

(18) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with CO in the Presence of Light

A quantity of 2 (50 mg, 0.052 mmol) was dissolved in 15 mL of MeCN. Carbon monoxide gas was bubbled through the solution while it was irradiated with a broad band UV-visible lamp for 2 h. The solution turned pale yellow within *ca.* 30 minutes;. An infrared spectrum taken after 10 min. showed both the v(C=N) stretches of the starting material, and CO bands. $IR(CaF_2, MeCN), cm^{-1}: 2343 (m), 2316 (w), 2121 (w), 2062 (w)$. The final solution after 2 h indicated the absence of the v(C=N) bands characteristic of the starting material and the presence of two very intense CO bands. $IR(CaF_2, MeCN), cm^{-1}: 2121 (vs), 2062 (vs)$. A vacuum was applied to remove the solvent, and as the volume was reduced, a dark blue solid began depositing on the sides of the vessel from a pale yellow solution. This easily redissolved in the pale solution upon agitation. The solution was reduced to a blue residue without a trace of yellow even though the solution did not

170

change color or darkened until dryness. The blue solid redissolves in MeCN to reform the yellow solution and vacuum application allows for cycling through the transformation repeatedly. After several cycles, the IR spectrum begins to change, indicating that the original compound is converting to a new more stable species. IR(CaF₂, MeCN), cm⁻¹: 2121 (m), 2062 (m), 2035 (vs). The reaction is extremely sluggish under ambient light conditions, but does eventually proceed to give a pale yellow solution at low concentration (e.g. 0.01 <u>M</u> is too concentrated). For reactions performed in room light, conversion to the pale yellow color occurred in ~ 2 h rather than in 30 min. The blue solid {IR(KBr, Nujol, very weak), cm⁻¹: 2330 (vw), 2302 (vw), 2048 (w), 1062 (s), 1034 (s)} is insoluble in THF and MeOH, but is soluble in acetone to give a solution IR with one band in the CO region (CaF₂, MeCN), cm⁻¹: 2032 (m). ¹H NMR of the blue solid (anaerobic, CD₃CN) showed only free CH₃CN at $\delta = 1.95$ ppm within 10 min. of sample preparation and data collection.

(19) Aerobic reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with CO and light.

A solution of 2 that had been exposed to O_2 was placed in an uncapped test tube and purged with CO in room light for 5 h. Infrared data indicated that the reaction was occurring in the same manner as the anaerobic photolysis reactions. IR(CaF₂, MeCN), cm⁻¹: 2121 (s), 2063 (s). The solution was allowed to stand for 9 days during which time the spectral properties changed. IR(CaF₂, MeCN), cm⁻¹: 2342 (s), 2121 (vs), 2063 (vs).

(20) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with CO in the dark.

A quantity of 2 (20 mg, 0.021 mmol) was dissolved in 10 mL of MeCN and covered with foil for 2 h, after which CO was bubbled through the solution in the continued absence of light for 4 h. IR data indicated that only a small amount of any CO products had formed. (CaF₂, MeCN), cm⁻¹: 2121 (vw), 2063 (vw).

(21) Thermal Reaction of [Rh₂(MeCN)₁₀][BF₄]₄ with CO in the dark.

An amount of 2 (20 mg, 0.021 mmol) was added to 10 mL of MeCN and the solution was covered with foil to keep out light for 2 h. The solution was then refluxed for 2 h with CO purging in the absence of light. A yellow solution was produced by addition of MeCN to the resulting residue formed by solvent evaporation. Infrared data indicated that the previously observed CO product was formed in moderate amounts. (CaF₂, MeCN), cm⁻¹: 2121 (m), 2063 (m).

(22) Reaction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with 10 equivalents of *i*-PrNC

A quantity of 2 (52 mg, 0.054 mmol) was dissolved in 5 mL of MeCN to which was added 49 μ L of isopropylisocyanide (0.540 mmol, 10.0 equiv.) whereupon the solution immediately turned bright yellow. A small amount of yellow solid precipitated within *ca*. 5 min. The solution was decanted and the solid was dried *in vacuo*. IR of the yellow solid, (CsI, Nujol), cm⁻¹: 2344(m), 2217 (m), 1062 (s, br). After standing for *ca*. 1 day, the solvent from the original solution was removed under vacuum to give a residue that appeared to be a mixture of orange and yellow solids; addition of MeCN to this residue produced an orange solution. IR(CaF₂, MeCN), cm⁻¹: 2343(m), 2317 (m), 2276 (vw), 2220 (w), 2175 (w). Hexanes (1 mL) and diethyl ether (~ 15 mL) were layered on the solution to produce a red microcrystalline solid tinged with a blue oil and a pale yellow solution. The solution was decanted and the solid was washed with THF and CH₂Cl₂, and finally MeOH to remove the blue component. Finally the residue was washed with diethyl ether $(2 \times 5 \text{ mL})$ and dried under vacuum. Addition of MeCN to the microcrystals gave a dark red solution. IR(CaF₂, MeCN), cm⁻¹: 2221 (w), 2193 (m), 2155 (m), 1954 (m), 1713 (m), 1276 (m), 1154 (vs, br). The red solution was layered over toluene to give a yellow solution and a small quantity of microcrystalline orange solid. The solution was decanted and subjected to a dynamic vacuum. IR of the orange solid, (CsI, Nujol), cm⁻¹: 2359 (m), 2342 (m), 2315 (m), 2286 (w), 2269 (m), 2258 (m), 1060 (s, br). As the solution volume was reduced, rings of a very dark solid reminiscent of the CO reactions filmed out on the sides of the flask until only a green-black solid remained. IR(CsI, Nujol), cm⁻¹: 2210 (w, br), 2144 (w), 1062 (s), 1030 (s). Redissolving this dark material in acetonitrile exhibited the IR properties (CaF₂, MeCN), cm⁻¹: 2192 (m), 2157 (s), 1273 (m), 1103 (w, br).

(23) Reaction of [Rh₂(MeCN)₁₀][BF₄]₄ with 10 equivalents of *n*-BuNC

A sample of 2 (27 mg, 0.028 mmol) was dissolved in 3 mL of MeCN. To this solution was added 29 μ L of *n*-butylisocyanide. The mixture was agitated to produce a yellow solution which was then layered with hexanes and diethyl ether (1 mL and ~ 8 mL respectively) to induce precipitation of a yellow solid. The solution was decanted and the solid was washed with diethyl ether (2 x 5 mL) and dried under a N₂ purge. IR(CsI, Nujol), cm⁻¹: 2337 (m), 2320 (shoulder), 2307 (shoulder), 2226 (m), 1061 (s, br). The decanted solution was reduced to a pink residue under vacuum. Addition of MeCN to this pink solid yielded a yellow solution which could once again be pumped to a bright pink residue. Layering with CH₂Cl₂ followed by diethyl ether (10 mL of each) did not produce a crystalline product.

C. Experimental, Crystallography [RhCl₂(NCCH₃)₄][BF₄]

Data Collection. Pertinent crystal data are summarized in Table 15. Large single crystals were grown by slow diffusion of toluene into a solution of the compound in acetonitrile. A hexagonal yellow crystal of dimensions $0.75 \times 0.41 \times 0.31$ mm was sealed in a quartz capillary and examined on a Rigaku AFC6S diffractometer equipped with graphite monochromated Mo K α ($\lambda \alpha = 0.71073A$) radiation. A random peak search indicated that the crystal diffracted well. The cell was indexed on 10 preliminary reflections which indicated a body-centered orthorhombic crystal system. An automatic Laue check verified this choice. An accurate high-angle cell used for data reduction was determined by 24 reflections in the range $38 < 20 < 40^{\circ}$. Three intensity standards were gathered every 150 reflections and displayed no decay during the course of data collection.

Structure Solution and Refinement. The data were collected in a nonstandard setting, and rotated into a standard setting using the matrix supplied by the PROCESS output in TEXSAN. The automatic TEXSAN software chose the acentric space group Iba2, but refinement in this space group revealed a large amount of correlation. Therefore the structure was resolved in the centric space group Ibam. The position of the Rh atom was determined by application of SHELXS-86,¹ and the rest of the atoms were located by initial alternating DIRDIF² refinement and Fourier maps until most of the structure was established, after which the least squares refinement procedure was used. All non-hydrogen atoms were refined anisotropically. Final refinement gave residuals of R = 0.032, and Rw = 0.055with the quality-of-fit indicator of 2.05 In the last cycle, 50 parameters were refined with 822 unique data and $F_{obs} > 3\sigma F_{obs}$ of 659. The shift/esd of the

Table 15. Crystal Data for [RhCl₂(MeCN)₄][BF₄]

Formula	RhCl ₂ N ₄ C ₈ H ₁₂ BF ₄	
Formula weight	424.83	
Space group	Ibam	
	6.220/1)	
а, А	6.239(1)	
b, Á	12.147(2)	
с, А	20.611(5)	
α, deg	90	
β, deg	90	
γ, deg	90	
v, A ³	1562(1)	
Z	4	
d _{calc, g/cm} 3	1.806	
μ (Μο Κα), cm ⁻¹	14.55	
Data collection instrument	Rigaku AFC6S	
Radiation (monochromated in incident beam)	Mo K $\alpha(\lambda \alpha = 0.71073 \text{\AA})$; graphite monochromated	
Temperature, °C	23 ± 2°	
Scan method	$\omega - 2\theta$	
Trans. Factors, max., min.	0.85, 1.00	
Rª	0.032	
R _w ^b	0.055	
$aR = \Sigma F_0 - F_c / \Sigma F_0 $		

 $bR_{w} = [\Sigma w | F_{o} | - | F_{c} |)^{2} / \Sigma w | F_{o} |^{2}]^{1/2}; w = 1/\sigma^{2} (|F_{o}|)$

final cycle was 0.02, and the highest remaining peak in the final difference Fourier map was 0.54 e^{-A^3} .

D. Results and Discussion

The proposed mechanism of the reversible photochemistry is presented in Figure 26. The solvent ligands have been left out for clarity, but each species is assumed to be fully solvated. The first step is homolytic bond cleavage in the presence of light to give two Rh(II) · radicals which have a lifetime of about 50 s according to *in situ* transient EPR experiments.³ The subsequent chemistry involves a series of redox reactions rather than radical reactions. The Rh(II) species is expected to become solvated by a MeCN ligand in the vacant coordination site thus inhibiting recombination. The reducing Rh(II) · species is capable of reducing an intact dinuclear (II,II) species to form Rh(III) and a reduced mixed-valence dinuclear Rh(I,II). This reduction by a photogenerated intermediate has been noted previously for $Ru_3(CO)_{12}$ and $CpMo(CO)_3Cl$ (Cp = cyclopentadienyl).⁴ Based on a combination of observation and procedure, we postulate that two of these mixed-valence species associate to form a mixed valence tetramer. $Rh_4(I,II,II,I)$. This is driven by the metal-metal bond formation between the d^7 centers of an unstable Rh(I)Rh(II) species. Precedence for this linear species is found in previous studies of dirhodium(I,II) isocyanides.⁵ In this work, the d^8 and d^7 centers were bridged so that the Rh(I) pieces could not dissociate after the metal-metal bond had formed. In the present system, unless the mixed-valence tetramer is isolated by precipitation, it quickly dissociates to form two Rh(I) fragments and the original $Rh_{\mathcal{I}}II,II$) species. Other reactions to reform the starting material include conproportionation of the Rh(I) and Rh(III), and radical recombination of Rh(II).

Figure 26. Proposed mechanism for the reversible photochemistry of [Rh₂(MeCN)₁₀][BF₄]₄

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Initiation:

 $Rh^{II}-Rh^{II}$ $hv \rightarrow 2Rh^{II}$.

Oxidation-Reduction: $Rh^{II} + Rh^{II} - Rh^{II}$ $2 Rh^{I} - Rh^{II}$ $2 Rh^{I} - Rh^{II}$ $Rh^{I} - Rh^{II} - Rh^{II}$

Termination:

Rh ^I +	$\mathbf{Rh}^{\mathbf{III}}$		Rh ^{II} —Rh ^{II}
$2 \mathrm{Rh}^{\mathrm{II}}$.		>	Rh ^{II} —Rh ^{II}

Figure 26

Much of this work was elucidated using sophisticated spectroscopic techniques and fast kinetic measurements at Los Alamos and the University of Texas at Austin. Our goal was to approach the same chemistry from the synthetic point of view in an attempt to reproduce these results under thermal conditions and to prepare the proposed intermediates to lend support to the postulated mechanism.

Electronic Spectroscopy of [Rh₂(MeCN)₁₀][BF₄]₄

It became apparent very early in this work that strict anaerobic conditions were required to avoid side reactions with O₂. Electronic spectra of samples prepared in air display not only the two authentic features (nm (ϵ , <u>M⁻¹</u> cm⁻¹)) at 468 (570) and 277 (22,000) for [Rh₂(MeCN)₁₀]⁴⁺, but also an additional feature at $\lambda_{max} = 365$ nm (1200). Samples prepared anaerobically in the dark display only the first two features. The conversion from the original spectrum to the aerobic spectrum was monitored by exposing a pure anaerobic sample to air and light and then recording the spectrum.

We also performed the irradiation experiment anaerobically. Figure 27 shows the visible region of a sample prepared in this manner. The solution was stored in the dark sample chamber and spectra were recorded every 5 min. The extra feature at $\lambda_{max} = 414$ nm was seen to disappear over time as the photochemical reaction pathway is shut down and the intermediates convert back to the starting material. These results are the same as those found at Los Alamos. Under their irradiation conditions, the 414 band was significantly more intense to the point that it overwhelmed the less intense 468 feature. Our results demonstrate the extreme photosensitivity of the compound, considering we used only ambient room light as a source of photons. The 414 band has been assigned to the Rh(I) species due to its

Figure 27. Electronic spectra of an anaerobically irradiated sample of [Rh₂(MeCN)₁₀][BF₄]₄ in MeCN solution recorded periodically without additional exposure to light



extremely high ε values and the location of the transition, both of which are typical of Rh(I) compounds.⁶

Although the photochemical reactivity had been established, we were curious as to whether the homolytic Rh-Rh bond cleavage and subsequent chemistry could be accessed thermally in the absence of light. Figure 28 depicts the spectra from a solution that had been refluxed in MeCN for several hours in the absence of light. Spectra were recorded on the hot solution and then monitored periodically as the solution cooled in the dark sample chamber. The transition at 414 nm was apparent early in the study and subsequently disappeared as the intermediates reacted to reform the original material.

Synthesis of Intermediates:

" [Rh₄^{I,II,II,I}(MeCN)₁₆]⁶⁺"

Elucidation and further support for the proposed photochemical mechanism would be most effectively achieved by using synthetic methods to access proposed intermediates. Individual preparation of the three most stable intermediates, Rh(I), Rh(III), and the proposed mixed-valence tetramer, would add convincing evidence for the proposed mechanism.

As mentioned in Chapter III of this dissertation, $[Rh_2(MeCN)_{10}][BF_4]_4$ possesses a single accessible irreversible reduction in the cyclic voltammogram. We attempted to exploit this process for the synthesis of a mixed-valence dinuclear species by bulk electrolysis. During this experiment, we were surprised to find that instead of a color change of the solution, a large amount of gray-green solid formed as a coating on the electrode and eventually settled to the bottom leaving behind a nearly colorless solution. It became apparent that the only difference between this experiment and

182

Figure 28. Electronic spectra displaying the thermal access to the Rh-Rh bond cleavage reaction in [Rh₂(MeCN)₁₀][BF₄]₄ in the absence of light



wavelength in nm

normal synthetic conditions was the large amount of supporting electrolyte that was present in the reaction. A variety of chemical reducing agents were used with the $Rh_2^{II,II}$ species while maintaining ~ 0.1 <u>M</u> salt concentrations Figure 29 summarizes the various methods used to produce dark colored precipitate that we postulate is the mixed-valence tetramer intermediate due to its similarity in color and luster to Gray and Mann's linear isocyanide species.⁵ That the starting material is supported solely by solvent complicates the isolation of the desired product, since there is a high probability of incorporating a non-innocent reducing agent into the coordination sphere. This was apparently the case with the tris(2,6dimethoxyphenyl) methyl radical as well as cobaltocene. Dave Morris at Los Alamos reported similar incorporation problems with using ferrocene as an internal standard in his electrochemistry experiments.

Two separate bulk electrolysis experiments were carried out to obtain enough of product to study by various spectroscopic means. Anaerobic isolation was virtually impossible with the electrochemical set-up in our laboratories, therefore the resulting products were filtered in air. Anaerobic dissolution of a sample of the brown solid in MeCN gave an orange solution whose electronic spectrum, shown in Figure 30, contained the same two components as the photochemical spectra, one absorption at $\lambda_{max} = 410$ nm due to Rh(I), and a shoulder at about 465 nm due to the Rh₂II,II cation, indicating that the brown solid contains a compound that dissociates into these compounds upon redissolution. Unfortunately, aerobic work-up clouded the issue of whether the authentic sample is paramagnetic or diamagnetic. Two separate samples of the aerobically isolated bulk electrolysis product gave EPR signals suggesting that they were paramagnetic. This was finally attributed to oxygen interaction when a rigorously aerobic sample prepared

185

Figure 29. Synthetic methods used in preparation attempts of the proposed mixed-valence tetramer, "[Rh₄I,II,II,I (MeCN)₁₆]⁴⁺"
$[Rh_2(MeCN)_{10}][BF_4]_4$ was combined with one of the following reducing agents at an elevated electrolyte concentration with the indicated results:



NaAce = Sodium acenaphthylenide

Figure 30. Electronic Spectrum of the proposed mixed-valence tetramer synthesized by bulk electrolysis redissolved in MeCN.



Figure 30

from the chemical reduction of $[Rh_2(MeCN)_{10}][BF_4]_4$ with NaEt₃BH displayed no EPR signal. This particular product is actually a slightly different form than the electrochemically generated compounds in that it is insoluble in MeCN.

Crystallization of a sample of reduced $[Rh_2(MeCN)_{10}]^{4+}$ was attempted by two different methods. Layering a cobaltocene solution over a solution of $[Rh_2(MeCN)_{10}][BF_4]_4$ produced crystals of the starting material and dark microcrystals of the product. The second technique employed electrocrystallization using the specialized cell represented earlier in Figure 25. This method was moderately more successful than the first, but gave only tiny needles that were not of x-ray quality. The latter procedure appears to be the most promising and will be pursued in future studies.

"[Rh^I(MeCN)₄]⁺"

One of the most commonly employed Rh(I) starting materials is $[RhCl(COD)]_2$. We proposed to abstract the halides from the complex and attempt to remove the cyclooctadiene ligands in the strongly coordinating MeCN solvent. A ¹H NMR of the product proved that the reaction did not proceed as hoped; although the halides were removed, the compound was the partially solvated cation, $[Rh(MeCN)_2(COD)]^+$. Future efforts should include substitution of the diene for two poorly ligating alkenes such as 1-hexene. These groups are removed more easily, or may be hydrogenated off to afford a better chance of accessing the Rh(I) solvate, $[Rh(MeCN)_4]^+$. This Rh(I) species ligated solely by solvent is likely to be extremely reactive and may be difficult to isolate, therefore extreme care and low temperatures must be used in future experiments.

"[Rh^{III}(MeCN)₆]³⁺"

Of the three target intermediate compounds, the Rh(III) species, $[Rh(MeCN)_6]^{3+}$ should be the most stable, due to the inert behavior of d⁶ species. Also, we rationalize that it would be easily prepared considering that $[Rh(H_2O)_6]^{3+}$ is already known.⁷ The obvious starting material for the preparation of a non-aqueous solvated Rh(III) species was the RhCl₃ hydrate. A variety of halide abstraction reagents were reacted with RhCl₃ · 3H₂O, including those that incorporate the halide into the counterion as well as those that precipitate the halide or remove it in a gaseous form. The reactions generally proceeded more easily if the RhCl₃ was first "digested" in MeOH to break up the polymeric network thereby creating a more reactive form of the complex.

The reaction with SbCl₅ produced bright yellow solids MeCN solutions of RhCl₃. A ¹H NMR spectrum of the product displayed two resonances, one at $\delta = 2.62$ ppm due to coordinated MeCN, and one at $\delta = 1.95$ ppm due to the ligands that had exchanged with the deuterated solvent. Two different X-ray data sets were collected on well-diffracting crystals, but we were unable to solve these data sets. The solution by various methods was always the same. Two large peaks which were likely the metals were bridged by a two atom unit in a linear fashion. The metals refined as either Sb or Rh, so these structures were abandoned. Antimony reagents are known to bind nitriles in the case of SbF₅,⁸ thus we decided to move to a slightly less potentially interfering agent for removing the halides.

Reactions with Ag^+ salts produced bright yellow solutions from which yellow solids were isolated. It soon became apparent that these solids were contaminated with substantial amounts of Ag^+ as evidenced by the color changes upon prolonged exposure to light, the reaction with the CsI windows

during infrared studies, and the deposition of Ag on the Pt electrodes during cyclic voltammetry experiments. A representative example of the latter is depicted in Figure 31. The silver salts, whether AgBF₄ or AgTFMS proved to have nearly identical solubility with the Rh-containing compound, so repeated recrystallizations were not successful at purifying the product. ¹H NMR spectral measurements, which are unaffected by the silver impurities, showed coordinated MeCN at $\delta = 2.62$ ppm and free MeCN at $\delta = 1.95$ ppm in various ratios depending on the time lapse between sample preparation and measurement. The infrared spectra taken on Nujol mulls on KBr windows showed, in addition to the [BF₄]⁻ or [TFMS]⁻ counterion, two stretches in the v(C=N) region, one very strong at 2351 cm⁻¹ and one medium intensity feature at 2323 cm⁻¹. Our inability to isolate a clean product from these reactions led to the use of acids as halide abstraction reagents.

Synthesis of [RhCl₂(MeCN)₄]⁺

The reaction of HBF₄ or HTFMS with $RhCl_3 \cdot 3H_2O$ results in dark yellow solutions that produce a large amount of bright yellow solid upon layering with hexanes and diethyl ether. A successful X-ray crystal structure revealed that only one chloride had been removed from the starting material to give the compound, $[RhCl_2(MeCN)_4][BF_4]$. This cation was reported previously, but had not been characterized crystallographically.⁹ Extended reaction times up to two weeks did not drive the reaction to a different product. Apparently the substitutionally inert nature of this Rh(III) compound inhibits the removal of the other two halides.

The $[RhCl_2(MeCN)_4]^+$ species is most likely the only product formed in the silver reactions and the antimony reactions as suggested by comparison of the spectra of the residues of these reactions with an authentic sample of Figure 31. Cyclic voltammetry of a halide abstraction product with RhCl₃ containing significant Ag⁺ impurity, in Volts vs. Ag/AgCl



Figure 31

[RhCl₂(MeCN)₄][BF₄]. ¹H NMR spectral measurements on a pure sample isolated from acidic preparation of this compound displayed the two resonances at $\delta = 2.62$ and $\delta = 1.95$ ppm observed for the other products, and the v(C=N) region of the infrared spectrum displayed the combination of the very intense stretch at 2355 and the medium intensity mode at 2322 cm⁻¹. This lower intensity mode was identified as the $v(C \equiv N)$ mode in the earlier report.⁹ Since this synthesis does not produce silver residues, CsI windows may be used to record the full IR spectrum; the v(Rh-Cl) stretch is visible in the far-infrared as a strong feature at 360 cm^{-1} . The quantitative electronic spectrum displays a transition at $\lambda_{max} = 414$ nm with a low ε value typical of Rh(III) complexes in the absence of ligands such as bpy^{10} as well as a higher energy transition at 235 nm ($\varepsilon = 32,000$). The 414 nm band compares favorably with 410 nm band reported earlier.⁹ Cyclic voltammetry experiments in 0.1 M TBABF₄ in MeCN displays two irreversible reductions at $E_{p,c}$ = -.23V and $E_{p,c}$ = -.54V referenced to Ag/AgCl. The irreversibility of these processes is logical since a Rh(II) species would be most stable as a dinuclear compound, and the structural rearrangement required would result in a completely irreversible redox process.

Several likely methods have been discussed for future efforts to prepare the Rh(III) solvate. One possibility is the dehydration of the $[Rh(H_2O)_6]^{3+}$ species. The difficulty with this is the isolation of this material in a pure form with no chlorides, and achieving total dehydration of the relatively inert metal center. A second possibility suggested by a collaborator at Los Alamos, is the use of RhBr₃ since the larger, more polarizable halides should be more easily removed. It should be noted that the $[RhBr_2(MeCN)_4]^+$ species is prepared by the reaction of RhBr₃ with AgClO₄, so forcing acidic conditions may be required to removed the additional bromides.⁹ Molecular Structure of [RhCl₂(MeCN)₄][BF₄]

Selected bond distances and angles are presented in Tables 16 and 17 respectively. Atomic positional parameters are contained in the Appendix. The ORTEP diagram in Figure 32 shows the molecular structure of $[RhCl_2(MeCN)_4][BF_4]$. Both the Rh and B atoms reside on crystallographic special positions- Rh is on a 2/m site, and B is on a 222 site, rendering the atoms one quarter occupied. The high symmetry of the octahedral rhodium and tetrahedral boron greatly reduces the number of unique atoms in each asymmetric unit. One F atom generates the other three in the anion, and the same is true for the acetonitrile ligand in the cation. The single unique Cl atom lies on a 2-fold axis at half occupancy. Within the octahedral coordination sphere of the cation, the chlorides occupy trans positions while the four acetonitrile ligands lie in the square equatorial plane as was proposed from the Raman spectroscopy in the original report.⁹ The $[BF_4]$. counterion is extremely well-determined with none of the common disorder associated with it. The high symmetry of this crystal can be easily seen by inspecting the ORTEP unit cell packing diagram, viewed down the a axis depicted in Figure 33.

Further Reactions with [RhCl₂(MeCN)₄][BF₄]

Although the partially solvated mononuclear species was not the desired product, this Rh(I) species is a versatile combination of stabilizing Clligands and more labile solvent. We propose that two of these units could be tethered by a bridging ligand such as mhp (mhp = methylhydroxypyridine) or dppm (dppm = 1,2-bisdiphenylphosphinomethane), and the two metals could then each be reduced by one electron to form a d^7 - d^7 system with a M-M bond. This type of reaction should prove quite interesting in the future and

atom	atom	distance	atom	atom	distance	
511	0 11	2 221 (1)	1	01	1 105/51	

Table 16. Selected Bond Distances in Å for [RhCl₂(MeCN)₄][BF₄]

		urscance			urstance
Rhl	C11	2.331(1)	N 1	C1	1.125(5)
Rh1	C11′	2.331(1)	C1	C2	1.463(6)
Rhl	N1	1.986(3)	B1	F2	1.339(4)
Rh1	N1'	1.986(3)	B1	F2′	1.339(4)
Rh1	N1''	1.986(3)	B1	F2′′	1.339(4)
Rh1	N1'''	1.986(3)	B1	F2′′′	1.339(4)

atom	atom	atom	angle
C11	Rh1	C11′	180.00
C11	Rh1	Nl	90.56(8)
C11	Rh1	N1 '	90.56(8)
C11	Rhl	N1''	89.44(8)
C11	Rh1	N1′′′	89.44(8)
C11'	Rh1	Nl	89.44(8)
C11′	Rh1	N1′	89.44(8)
C11′	Rh1	N1''	90.56(8)
C11′	Rh1	N1'''	90.56(8)
N 1	Rhl	N1'	88.3(2)
N 1	Rh1	N1''	91.7(2)
N 1	Rhl,	N1'''	180.00
N1′	Rh1	N1''	180.00
N1′	Rhl	N1 ′ ′ ′	91.7(2)
N1''	Rhl	N1'''	88.3(2)
Rhl	N 1	Cl	176.2(3)
N1	C1	C2	177 .9(4)
F2	B1	F2′	114.0(4)
F2	B1	F2′′	106.8(4)
F2	B1	F2′′′	107.7(4)
F2′	B1	F2′′	107.7(4)
F2′	B1	F2′′′	106.8(4)
F2′′	В1	F2′′′	114.0(4)

Table 17. Selected Bond Angles in degrees for [RhCl2(MeCN)4][BF4]

Figure 32. ORTEP diagram of the cationic component of [RhCl₂(MeCN)₄][BF₄]



Figure 33. ORTEP Unit Cell Packing Diagram of [RhCl₂(MeCN)₄][BF₄], viewed down the A axis



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may present a different way of accessing dinuclear species for the late transition metals.

Photochemical Reactions of [Rh₂(MeCN)₁₀][BF₄]₄ with CO

Since the preparation of the proposed photochemical intermediates had not proceeded unequivocally in any case, we set out to trap these intermediates in a derivatized form. A photolyzed solution of $[Rh_2(MeCN)_{10}][BF_4]_4$ reacts with CO (g) at r. t. to give a pale yellow solution. A solution IR of this species indicates that the product that has been formed is the previously reported but very poorly characterized *cis*. $[Rh(CO)_2(MeCN)_2]^{+,11}$ Reducing this solution to a residue under vacuum deposits a blue solid as the square planar Rh(I) species associate.¹¹ The transformation from the yellow solution species to the blue solid may be effected several times, but with each cycle of pumping, a new stretch in the IR at 2035 cm⁻¹ grows in intensity. The identity of this new species has not yet been elucidated. Such extremely high energy stretches for v(CO) (2121 and 2062 cm⁻¹ for *cis*-[Rh(CO)_2(MeCN)_2]⁺) are uncommon, but not unknown. Extremes of 2204 cm⁻¹ have been reported for Ag(CO)B(OTeF_5)_4 in which the CO is said to be acting entirely as a Lewis base with no π -acid character.¹²

The importance of this reaction is that it requires access to the photochemical pathway in order to occur as evidenced by the lack of appreciable reactivity observed for the solutions kept in the dark. Ambient light results in much slower reactions than the strongly photolyzing conditions with a broad band UV-visible source. The same results may be achieved thermally by purging a refluxing MeCN solution of $[Rh_2(MeCN)_{10}][BF_4]_4$ in the dark, but photolysis remains the best method of preparing the yellow solution. The presence of the Rh(I) species in the photolyzed solutions was verified by trapping out the cation with CO, and the Rh(III) species is necessarily present for charge balance. Successful separation of the two species and characterization by X-ray analysis is important as these products strongly support the photochemical mechanism.

Reactions with isocyanides

Reactions with isocyanides which are isoelectronic with CO were carried out in hopes of discovering similar chemistry. Indeed 10 equivalents of either isopropylisocyanide or n-butylisocyanide react with solutions of $[Rh_2(MeCN)_{10}][BF_4]_4$ to instantaneously produce pale yellow solutions as in the CO reactions. The isocyanides modify the nature of the products sufficiently such that MeCN ligands were observed in the solution IR spectra in contrast to the CO spectra in which these stretches were conspicuously absent, even though crystallography has established their presence. The nitrile and isocyanide stretches fall close together, so specific formulations are not easily derived from these spectra other than concluding that the compounds contain both ligand types. Evaporation of the isocyanide reaction solutions does not produce the dark colors of the CO solutions, instead, red (i-PrNC) or pink (*n*-BuNC) microcrystalline solids were obtained. The *i*-PrNC solutions finally produced dark solids similar to the solid CO products, but it is apparent that the chemistry of these ligands is not identical to the CO reactions. Firstly, light is not required to initiate the reaction, and secondly, the $[Rh(NCCH_3)_2(CNR)_2]^+$ compounds are not known. The most common isocyanide Rh(I) species are homoleptic compounds of the form, $[Rh(CNR)_4]^+$ which are easily prepared by addition of excess isocyanide to $[Rh(CO)_2Cl_2]_2$.¹³ Partial adducts may be prepared by stoichiometric substitution of the carbonyl starting material, or by measured addition of a

new ligand to the homoleptic isocyanide material,^{13a,14} but the only thermodynamically stable bis-isocyanide complexes are the dinuclear bridged systems of Balch where the ligands are forced to adopt a trans disposition.¹⁵ Square planar Rh(I) isocyanide compounds do interact in the solid state along a metal-metal vector which may explain the final dark solid produced in the current reactions.^{5a} Unfortunately, the spectral data of any of the aforementioned compounds does not resemble that of the present chemistry, so identification of the products has not yet been established. Additional studies to elucidate these compounds are in order.

E. Summary

The photochemistry of $[Rh_2(MeCN)_{10}][BF_4]_4$ was seen to be accessible under ambient light and heat conditions in our laboratories. Although the synthesis of the proposed intermediates was not entirely successful thus far, the results achieved will be invaluable in guiding future efforts in these areas. The Rh(III) species is expected to be the most likely intermediate to be isolated and fully characterized; crystallization of the mixed-valence tetramer is likely to be much more difficult. In another approach to verifying the presence of solvated Rh(I) and Rh(III) cations, we used CO trapping experiments to selectively react with the Rh(I) intermediate which stabilizes it but does not interfere with the Rh(III) complex. Reactions with isocyanides have not been as promising in these derivative reactions. Both these and the subsequent chemistry of the CO solutions will be pursued.

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CHAPTER V

STRATEGIES FOR THE SYNTHESIS OF OTHER SOLVATED

DINUCLEAR TRANSITION-METAL COMPLEXES

A. Introduction

The success that was encountered in the preparation of the dirhodium acetonitrile system spurred us to investigate the synthetic applicability of our general methodology to other transition metals to establish practical methods of preparing a wide number of dinuclear solvated starting materials.

Extrapolation to the dirhenium system was accomplished by other group members who established three different routes to access the decakisacetonitrile dirhenium system. The initial approach took advantage of the first successful method of synthesizing $[Rh_2(MeCN)_{10}][BF_4]_4$ from $Rh_2(OAc)_4(MeOH)_2$. The dirhenium tetraacetate complex is extremely insoluble, so the tetrabutyrate was used. $Re_2(O_2CR)_4Cl_2$ compounds possess axial chlorides which must be removed with AgBF₄ prior to reaction of the carboxylate with the triethyloxonium reagent. A reduction occurs during this reaction to yield the triply bonded solvated species, $[Re_2(MeCN)_{10}]^{4+}$ in moderate yields:¹

 $Re_{2}(O_{2}CR)_{4}Cl_{2} + 2AgBF_{4} \xrightarrow{MeCN} [Re_{2}(O_{2}CR)_{4}(MeCN)_{2}][BF_{4}]_{2} + 2AgCl(s)$ Equation 11

 $[\operatorname{Re}_{2}(O_{2}CR)_{4}(\operatorname{MeCN})_{2}][BF_{4}]_{2} + \operatorname{Et}_{3}OBF_{4} \xrightarrow{\operatorname{MeCN}} [\operatorname{Re}_{2}(\operatorname{MeCN})_{10}][BF_{4}]_{4}$ Equation 12

The tetrapositive charge is common among the three known dinuclear acetonitrile cations, Mo, Rh, and Re, in spite of the differing M-M bond multiplicities. It may be that the dimetal units are unable to stabilize charges of higher magnitude than 4+.

Protonation reactions also may be used to access the dinuclear rhenium solvate. The first method involved halide abstraction from the common starting material, $[\text{Re}_2\text{Cl}_8]^2$, with HBF₄ as is shown below.²

 $[\text{Re}_2\text{Cl}_8]^{2-} + \text{HBF}_4 \xrightarrow{\text{MeCN}} [\text{Re}_2(\text{MeCN})_{10}][\text{BF4}]^4 + 8 \text{ HCl}(g)$ Equation 13

This chemistry also involves *in situ* reduction from the Re(III) starting material; some advantages of this reaction are that it is a higher yield one-pot synthesis and that it requires one less step as it begins with $[\text{Re}_2\text{Cl}_8]^{2-}$ and not with $\text{Re}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ which itself must be synthesized from $[\text{Re}_2\text{Cl}_8]^{2-}$. Without question, however, the best method for preparing $[\text{Re}_2(\text{MeCN})_{10}]^{4+}$ is directly, in the correct oxidation state, by protonation of all the ligands on mixed halide-phosphine compounds of the form, $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$.²

$$\frac{\text{MeCN}}{\text{Equation 14}} = \frac{\text{MeCN}}{\text{Equation 14}} \begin{bmatrix} \text{Re}_2(\text{MeCN})_{10} \end{bmatrix} \begin{bmatrix} \text{BF4} \end{bmatrix} 4 + 4 \text{ HCl}(g) + 4 \text{ HPR}_3$$

No single synthetic method is likely to be appropriate for preparing solvated dinuclear cations for every transition element, and as demonstrated in both the Rh and Re chemistry, and there is often more than one successful route to the final target complex. Investigation of other metal systems including divalent Cr, Ir, Ru, Mo, and Os has seen the application of a variety of synthetic methods as the identity of convenient starting materials changes. The results of these studies are presented herein.

B. Experimental, Synthesis

(1) Reaction of $Cr_2(OAc)_4 \cdot H_2O$ with Et_3OBF_4

Rigorously anaerobic and moisture-free conditions were maintained for this extremely air-sensitive reaction. An amount of anhydrous $Cr_2(OAc)_4$ (100 mg, 0.294 mmol) obtained from Aldrich was stirred at room temperature with 5 mL of Et_3OBF_4 (1 M in CH_2Cl_2) and 10 mL of freshly distilled MeCN for a week. The rose colored starting material was insoluble in MeCN, nevertheless, it reacted and turned blue upon addition of the triethyloxonium solution, and became dark purple over the course of several days. The solution was then heated for 3 days after which it was cooled which produced peach colored crystals at the neck of the flask and a red-purple solution. Layering diethyl ether (~ 15 mL) on the decanted solution produced more peach crystals admixed with purple needles. Separation of these two species to get a single pure product was achieved by addition of MeCN which selectively dissolved the purple product but left behind the orange crystals. The solution was decanted and the orange solid pumped to dryness. No pure sample of the purple species was isolated. IR of the peach crystals, (KBr, Nujol), cm^{-1} : 2330 (vs), 2301 (vs), 1023 (vs, br), 959 (vs), 470 (m), 445 (vs). ¹H NMR (CD₃CN₂): $\delta = 1.95$ ppm (singlet, free CH₃CN). Brief exposure to air turns the orange solutions and solids green, presumably due to oxidation reactions.

(2) Reaction of $IrCl_3$ with $TlPF_6$

Iridium trichloride trihydrate was obtained from Aldrich. A quantity of $IrCl_3 \cdot 3H_2O$ (110 mg, 0.312 mmol) was reacted with $TlPF_6$ (380 mg, 1.09 mmol, 3.5 equiv.) at r.t. in 10 mL of MeCN. Ambient conditions did not promote reaction, therefore the reaction was heated to reflux for 3 days. The resulting yellow solution was separated from a large amount of white solid by filtration. The solution was then layered with 10 mL of diethyl ether which caused an oily solid to form.

(3) Reaction of IrCl₃ with SbCl₅

The acetonitrile complexed form of antimony pentachloride was prepared according to the literature.³ An amount of $IrCl_3 \cdot 3H_2O$ (200 mg, 0.567 mmol) was refluxed in 5 mL of MeOH overnight and pumped to a residue. To this was added 5 mL of MeCN and 559 mg of SbCl₅ · 1.14 MeCN (1.616 mmol, 2.85 equiv.) and the combined reagents were stirred at reflux temperatures for 4 days. This produced a brown solution with a small amount of brown precipitate. The solution was filtered anaerobically. Addition of 10 mL of CH₂Cl₂ did not form a precipitate, and 10 mL of diethyl ether oiled the product. After these nonvolatile solvents were removed by evaporation, the volume of MeCN was increased by 3 mL and CH₂Cl₂ (~ 12 mL) was layered underneath to precipitate a brown solid and a deep orange solution. Decanting the solution and reducing the volume produced more brown solid. This reaction did not appear to be particularly promising for the formation of Ir(III) species which are typically pale yellow compounds.⁴

(4) Reaction of IrCl₃ with AgBF₄

In a typical reaction, a quantity of $IrCl_3 \cdot 3H_2O$ (200 mg, 0.567 mmol) was refluxed in MeOH for 12 h and reduced to a residue under vacuum. The solid was dissolved in 5 mL of MeCN and decanted into 331 mg of AgBF₄ (1.70 mmol, 3.0 equiv.). This mixture was refluxed for 24 h, which produced a yellow solution and a tan solid. Several isolation procedures were attempted, each involving the precipitation of additional AgCl by either reduction of the volume or by addition of a precipitating solvent. Final isolation of the Ircontaining product required pumping the solution to a residue. IR (CsI, Nujol), cm⁻¹: 2305 (m), 2280 (m), 1290 (m), 1070 (s, br), 520 (m), 385 (w). ¹H NMR (CD₃CN), $\delta = 2.84$ (s, coordinated <u>CH₃CN</u>), 1.95 ppm (s, free <u>CH₃CN</u>), approximately 1:10 ratio. The presence of Ag-containing impurities was obviated in the cyclic voltammetry by a catalytic reaction with the Pt electrode at $E_{p,c} = +0.26V$.

(5) Reaction of IrCl₃ with AgTFMS

A sample of $IrCl_3 \cdot 3H_2O$ (309 mg, 0.876 mmol) was refluxed in 5 mL of MeOH for two hours to effect dissolution. The resulting olive green solution was reduced to a residue under vacuum and redissolved in 5 mL of MeCN. This solution was then transferred into a vessel containing AgTFMS (.676 mg, 2.63 mmol) and refluxed for 1 week. (It is important that the Ag reagent is not predissolved and added to the IrCl₃ because silver salts will decompose in light.) After heating was ceased, the solution was a yellow color and a pale tan solid was present. The solution was decanted from the AgCl solids, and the volume was reduced to about ~ one-half. Toluene was added (8 mL) and the solution was chilled to -20°C. After precipitation, the bright yellow solid was seen to be admixed with white AgTFMS. Separation was not achieved in spite of repeated recrystallization. IR (KBr, Nujol), cm⁻¹: 2330 (s), 2309 (m), 1414 (s), 1365 (m), 1273 (vs), 1224 (s), 1146 (vs), 1034 (vs), 639 (vs), 560 (m), 510 (m). UV-visible (λ_{max} 316 nm, shoulder at 280 nm). The far-infrared was not recorded as the silver-containing impurities react with the CsI cells. ^{1}H NMR (CD₃CN, anaerobic): $\delta = 2.82$ ppm (s, coordinated <u>CH₃CN</u>), 1.95 ppm (s, free \underline{CH}_3CN), approximately 10:1 ratio.

(6) Reaction of IrCl₃ with HBF₄

To an amount of $IrCl_3 \cdot 3H_2O$ (213 mg, 0.604 mmol) was added 10 mL of MeOH which was refluxed until the solid had completely dissolved. This solution was reduced to a residue under vacuum to which 10 mL of MeCN and 0.8 mL of HBF₄ were added. This solution was refluxed for 4 days after which the reaction was cooled, reduced to *ca*. 2 mL, and filtered to remove a minor amount of gray precipitate. To the filtrate was added 5 mL of CH₂Cl₂, and the solution was chilled to -40 °C. Further attempts to precipitate a solid with toluene, ether, CH₂Cl₂, or combinations thereof led only to oils or sticky products. IR (CsI, Nujol), cm⁻¹: 2350 (w), 2312 (w), 1070 (m, br), 1040 (m), 330 (m).

(7) Reaction of RuCl₃ with TlPF₆

Ruthenium trichloride hydrate was obtained through a platinum metal loan from Johnson-Matthey. The amount of hydration was calculated to be 2.17 waters per ruthenium based on the metal analysis listed on the bottle. The same starting material was used in subsequent reactions unless otherwise indicated.

A quantity of RuCl₃ hydrate (100 mg, 0.406 mmol) was refluxed with TlPF₆ (523 mg, 1.50 mmol, 3.69 equiv.) in 10 mL of MeCN for 5 days. The original dark brown solution and suspension was converted to an intense blue-purple color before finally becoming an intense blue color. ($\lambda_{max} = 578$ nm, shoulder at 318 nm) TlCl was observed as a precipitate at the bottom of the flask, and additional amounts came out of the solution as the volume was reduced. Diethyl ether (8 mL) was layered on the MeCN solution in an attempt to isolate a blue solid, but exposure to air led to decomposition as evinced by the solution changing to dark purple. This purple solution

produced both purple and white solids which were not possible to separate. Separation attempts were carried out in air, and the purple solution eventually decomposed to a peach solution.

(8) Reaction of RuCl₃ with AgBF₄

Quantities of RuCl₃ hydrate (110 mg, 0.446 mmol) and AgBF₄ (259 mg, 1.33 mmol, 2.98 equiv.) were stirred in 8 mL of MeCN. The initial solution was dark brown in color, but eventually turned olive green within 5 h. The final dark blue solution was filtered and chilled after the addition of 8 mL of diethyl ether. A large amount of dark blue solid precipitated after several additions of diethyl ether to give a dichroic purple/red solution. After the mother liquor was decanted from the solid, the product was washed with diethyl ether (3 x 5 mL) and dried *in vacuo*. A ¹H NMR spectrum (CD₃CN, anaerobic): $\delta = +2.49$ ppm (s), displayed no sign of free CH₃CN, and the sample appeared to be diamagnetic. IR (CsI, Nujol), cm⁻¹: 2334 (w), 2305 (w), 1282 (m), 1050 (vs, br), 520 (m), 260 (vw). UV-visible (MeCN) λ_{max} at 579 nm, shoulders at 319 and 267 nm. The solid was free of Ag⁺ impurities as judged by cyclic voltammetry; dilute solutions displayed no interaction with the Pt electrode.

(9) Reaction of RuCl₃ with HBF₄

A sample of RuCl₃ hydrate (113 mg, 0.458 mmol) 0.5 mL of HBF₄/diethyl ether complex, 5 mL of MeCN, and 20 mL of CH_2Cl_2 were stirred together and refluxed for 7 days. The resulting solution which was red with a brown precipitate was filtered and extracted with hexanes to remove grease; finally the volume of the solution was reduced. CH_2Cl_2 (3 mL) was added to encourage precipitation, but this turned out to be

immiscible with the solution. MeCN was then added until the layers mixed. No solid was obtained from these efforts.

(10) Reaction of RuCl₃ with HTFMS

An amount of RuCl₃·hydrate (254 mg, 1.03 mmol) was stirred and refluxed in 8 mL of MeCN with 1 mL of HTFMS for 4 days. A dark red solution and a brown solid resulted. Chilling the solution to 0 °C yielded an orange-brown solution with a finely divided black suspension. The solution was filtered, the volume reduced to about one-half, and a 1:1 mixture of CH_2Cl_2 : diethyl ether (~ 10 mL) was added with chilling to -40 °C to encourage precipitation. After this treatment, the solution turned orange and a beige precipitate formed. No further work was done since the prior work-up seemed to have changed the identity of the original product.

(11) Reactions of anhydrous RuCl₃

RuCl₃ anhydrous (160 mg, 0.771 mmol) was refluxed in 5 mL of MeOH for two days. The solid was totally insoluble in this medium.

(12) Reaction of Ru₂(OAc)₂(CO)₄(MeCN)₂ with Et₃OBF₄

The ruthenium starting material was prepared according to literature methods.⁵ A sample of $Ru_2(OAc)_2(CO)_4(MeCN)_2$ (108 mg, 0.210 mmol) was refluxed with 5 mL of a 1 <u>M</u> solution of Et₃OBF₄ in CH₂Cl₂ and 10 mL of MeCN for 4 days. The original bright yellow solution turned a bright orange color. The volume of the solution was reduced and diethyl ether (~ 8 mL) was added, but this did not produce a solid. Further efforts to isolate a solid by addition of toluene or CH₂Cl₂ yielded intractable oils.

(13) Reaction of Ru₂(OAc)₄Cl with HBF₄

Ruthenium tetraacetate monochloride was prepared according to the literature method.⁶ A quantity of $Ru_2(OAc)_4Cl$ (72 mg, 0.152 mmol) was refluxed with 1 mL of HBF₄/diethyl ether complex in diethyl ether and 5 mL of MeCN for 2 weeks. The resulting red solution was filtered to remove a small amount of brown precipitate at the bottom, the solution volume was reduced slightly and finally layered with hexanes and diethyl ether (1 mL and 10 mL respectively). This work-up produced a small amount of colorless crystals. Further attempts to isolate a colored product from the solution led only to oils. (UV-visible of the red solution, $\lambda_{max} = 367$ nm).

(14) Reaction of Ru₂(OAc)₄Cl with HTFMS

 $Ru_2(OAc)_4Cl$ (102 mg, 0.215 mmol) was refluxed with 5 mL of MeCN and 0.5 mL of HTFMS for 24 h. The resulting red-orange solution was reduced in volume by one-half and 3 mL of CH_2Cl_2 was added to induce precipitation. Additional CH_2Cl_2 (2 mL) was added with no effect, but 3 mL of diethyl ether precipitated a tan-orange solid. Additional amounts of diethyl ether and subsequent chilling to -40 °C yielded a brown solid, an orange solution, and small gold crystals likely to be the known Ru(II) cation, $[Ru(MeCN)_6]^{2+}$, judging by the pale color. No further efforts were made to isolate a pure product from this complicated mixture.

(15) Reaction of [Ru₂(OAc)₄(THF)₂][BF₄] with HBF₄

The literature procedure was followed to prepare the axially solvated diruthenium tetraacetate.⁷ [Ru₂(OAc)₄(THF)₂][BF₄], (102 mg, 0.154 mmol), 0.5 mL of HBF₄, and 5 mL of MeCN were refluxed together for 2 days to yield a translucent red solution. Addition of 5 mL of CH₂Cl₂ followed by 5 mL of

diethyl ether and chilling of the solution to -40 °C precipitated orange-brown and white solids from an orange solution. As in Reaction (14), no solid could be isolated.

(16) Thermal Reaction of [NH₄]₅[Mo₂Cl₉] with HBF₄

A quantity of $[NH_4]_5[Mo_2Cl_9]$ (205 mg, 0.034 mmol), prepared according to the literature procedure,⁸ was refluxed with 0.5 mL of HBF₄ and 5 mL of MeCN. The reaction turned green within ~ 10 min. and after 16 h of reflux, the solution color was yellow-gold. Presumably the extended heating period led to decomposition.

(17) Reaction of [NH₄]₅[Mo₂Cl₉] with HBF₄ at Room Temperature

An amount of $[NH_4]_5[Mo_2Cl_9]$ (144 mg, 0.240 mmol) was stirred at r.t. with 0.5 mL of HBF₄/diethyl ether complex and 5 mL of MeCN. After 24 h, the solution had turned green-blue, which did not resemble the deep blue of the target complex, $[Mo_2(MeCN)_{10}]^{4+}$. Extended stirring for several weeks still did not produce any further color change. Work-up with CH₂Cl₂ and diethyl ether produced an extremely oily forest green solid that could not be dried adequately for characterization purposes.

(18) Reaction of K₄[Mo₂Cl₈] with HBF₄

A sample of $K_4[Mo_2Cl_8]$ (100 mg, 0.158 mmol), synthesized by literature methods,⁹ was reacted with 0.5 mL of HBF₄ and 5 mL of MeCN and stirred at r.t. for 2 days to yield a green solution over a large amount of light blue solid. The green solution was decanted from the solid which was washed with diethyl ether and pumped to dryness. A ¹H NMR spectrum of the solid in CD₃CN displayed too many resonances to be the pure solvated complex. Addition of diethyl ether (~ 8 mL) to the green solution yielded a dark blue-green solid that did not resemble the color of $[Mo_2(MeCN)_{10}]^{4+}$.

(19) Reaction of K₄[Mo₂Cl₈] with HTFMS in the presence of Propionitrile

An amount of $K_4[Mo_2Cl_8]$ (100 mg, 0.158 mmol) was combined with 5 mL of EtCN and 1.5 mL of HTFMS. The mixture was refluxed for 1.5 h to yield a green solution. Addition of 20 mL of CH_2Cl_2 led to a green solution and a pale colored suspension.

(20) Reaction of $Mo_2Cl_4(Me_2S)_4$ with HBF₄

Tetrachlorotetrakis(dimethylsulfide)dimolybdenum(II) was prepared according to the literature method.¹⁰ An amount of $Mo_2Cl_4(Me_2S)_4$ (.105 mg, 0.180 mmol) was refluxed with 10 mL of MeCN and 0.8 mL of HBF₄/ diethyl ether complex for 11 days. Prior to addition of HBF₄, the initial solution was blue, but within 24 h of reacting with HBF₄ under reflux conditions, the solution began to turn green. Prolonged reaction did not cause formation of a blue solution. Hexanes and diethyl ether (1 mL and 10 mL respectively) were added to precipitate a sticky solid that contained several different shades of green. Attempts to grind a sample for an infrared spectrum led to a sticky solid that was immiscible with Nujol.

(21) Reaction of K₄[Mo₂Cl₈] with NaBPh₄

A sample of $K_4[Mo_2Cl_8]$ (99 mg, 0.157 mmol) and 430 mg of NaBPh₄ (1.26 mmol, 8.02 equiv.) was stirred at r.t. for 3 days. An intense blue solution and a large amount of white precipitate ensued. The NaCl was removed by filtration (184 mg, 20.0 equiv.), but the solution was accidentally exposed to air and it subsequently decomposed.

(22) Reaction of OsCl₃ with AgTFMS

A quantity of commercially available $OsCl_3$ (200 mg, 0.674 mmol) was stirred at r.t. with AgTFMS (572 mg, 2.23 mmol, 3.31 equiv.) in 10 mL of MeCN. Within 10 min., the solution turned brown, and within 24 h, the solution was a very dark purple color with no precipitate present. Addition of toluene and chilling to -40 °C precipitated a large amount of blue-gray solid. The solution was filtered and reduced under vacuum to a sticky residue. Recrystallization from MeCN/CH₂Cl₂ did not yield a dry solid.

(23) Reaction of $[n-Bu_4N]_2[Os_2Cl_8]$ with HBF₄

Octachlorodiosmate was prepared according to the method reported by Walton *et al.* ¹¹ A sample of the green $[n-Bu_4N]_2[Os_2Cl_8]$ (91 mg, 0.079 mmol) was treated at r.t. with 0.5 mL of HBF₄ and 5 mL of MeCN for 4 days with no change in color. Chilling the solution to -40 °C produced a tan precipitate and a green-gold solution. Addition of CH₂Cl₂ and diethyl ether (5-8 mL each) produced only immiscible oils.

(24) Reaction of $[n-Bu_4N]_2[Os_2Cl_8]$ with 8 equivalents of AgBF₄

The solids, $[n-Bu_4N]_2[Os_2Cl_8]$ (85 mg, 0.074 mmol) and AgBF₄, (115 mg, 0.591 mmol, 7.99 equiv.) were stirred in 5 mL of MeCN for 6 days. A brown precipitate formed in an opaque solution. The solution was filtered through Celite several times to remove the precipitate, and then layered with hexanes (1 mL) and diethyl ether (8 mL). A finely divided brown solid precipitated, leaving behind a gold solution which was decanted and saved.

An IR spectrum of the first brown solid displayed a small amount of MeCN and a small feature in the region for an v(Os-Cl). The solution was extracted three times with hexanes (5 mL portions) to remove oil that contaminated the solution, and then layered with toluene to again yield a brown precipitate. A ¹H NMR spectrum of the brown solid displayed only a small amount of free MeCN and a substantial amount of [*n*-Bu₄N]⁺.

(25) Reaction of $[n-Bu_4N]_2[Os_2Cl_8]$ with HTFMS in the presence of Propionitrile

A sample of $[n-Bu_4N]_2[Os_2Cl_8]$ (132 mg, 0.115 mmol) was refluxed with 5 mL of EtCN and 1.5 mL of HTFMS for 90 min. The resulting solution was golden brown. Addition of 20 mL of CH_2Cl_2 caused only a small amount of brown oil to form at the bottom; addition of 10 mL of diethyl ether had no effect.

(26) Reaction of $Os_2(OAc)_4Cl_2$ with AgTFMS and Me₃SiTFMS

Diosmium tetraacetate dichloride was prepared according to the method of Wilkinson *et al.* ¹² A sample of $Os_2(OAc)_4Cl_2$ (52.6 mg, 0.077 mmol) was stirred with 39 mg of AgTFMS (0.152 mmol, 1.97 equiv.) in 5 mL of MeCN. This produced an opaque blue-black solution with a slight red dichroism. A fine precipitate was present, but no significant amount of AgCl was observed. Filtration to remove the finely divided precipitate did not work well because of the large porosity of the frit. Me₃SiTFMS (1 mL) was added, and the solution was refluxed for a week. The resulting solution was an opaque purple-black that appeared red in color if light was passed through the solution from behind. The volume was reduced to ~ 2 mL and toluene (3 mL) was layered underneath. Black microcrystals formed upon chilling the solution to -40 °C. The solution was decanted and the crystals were pumped to dryness. IR (KBr, Nujol), cm⁻¹: 2295 (m), 1710 (m), 1273 (vs), 1234 (vs), 1196 (vs), 1168 (s), 1034 (vs), 639 (vs).

(27) Reaction of $Os_2(OAc)_4Cl_2$ with HBF_4 in the presence of Propionitrile

A sample of $Os_2(OAc)_4Cl_2$ (102 mg, 0.148 mmol) was refluxed with 0.7 mL of HBF₄ and 5 mL of EtCN for 24 h with stirring to effect complete dissolution of the starting material. The resulting solution which was green/red dichroic was layered with hexanes and diethyl ether (1 mL and ~ 8 mL respectively) with no precipitation. The solvent was then removed under vacuum and 10 mL of diethyl ether was added to the solution without any noticeable change. When this solvent was removed under vacuum, 0.5 mL of triethylorthoformate was added to aid in dehydration of the solution. Subsequent layering with hexanes (1 mL) and diethyl ether (~ 10 mL) on this solution produced two layers; the upper layer was brown and the bottom layer was green. A small amount of oily solid precipitated, but the ¹H NMR spectrum showed it to be a highly impure compound. Subsequent work-up did not yield a clean product.

(28) Reaction of $Os_2(OAc)_4Cl_2$ with HBF₄ in the presence of Acetonitrile and Dichloromethane

In an effort to isolate a solid from these reactions, dichloromethane was added to the reaction solution in hopes of precipitating the product as it was formed. A quantity of $Os_2(OAc)_4Cl_2$ (137 mg, 0.199 mmol) was refluxed and stirred together with 16 mL of either 1:1 or 3:1 CH_2Cl_2 : MeCN and 1 mL of HBF₄ for 6 days. The initial brown insoluble starting material formed a
dark purple solution after *ca.* 1 day. The volume of the reaction solution was reduced under vacuum, and hexanes and diethyl ether (1 mL and 20 mL respectively) were layered on the MeCN/CH₂Cl₂ solvent mixture to isolate the product. A large amount of dark solid precipitated, leaving behind a relatively dilute red-purple solution which was decanted off. Continued workup was carried out in air. Acetone (10 mL) was added to partially dissolve the solid, producing a dark purple solution which was decanted and filtered. This procedure was repeated to obtain two similar purple solutions which were combined. Hexanes were added to the solution to precipitate product A; yield, 25 mg. The remaining original solid was dissolved in copious amounts of acetone to yield a blue solution. The volume was reduced, and a suspended solid was easily collected by filtration; yield of product B, 65 mg.

<u>Product A</u>: IR (CsI, Nujol), cm⁻¹: 2294 (m), 1641 (m), 1531 (m), 1064 (vs), 1022 (vs), 781 (m), 688 (m), 520 (m). ¹H NMR (CD₃CN): δ = 8.58 ppm (s, 3.74 H), 6.07 (s, 7.65 H), 2.71 (s, 0.96 H), 2.19 (s, unintegrated), 2.08 (s, unintegrated), 1.95 ppm (s, unintegrated). UV-visible (MeCN) $\lambda_{max} = 572$ nm. <u>Product B</u>: IR (CsI, Nujol), cm⁻¹: 2330 (w), 2298 (m), 1653 (w), 1539 (s), 1064 (vs), 1028 (vs), 680 (m), 522 (w). ¹H NMR (CD₃CN): δ = 12.15 (s, br), 2.48 H), 9.7 (s, br, 6.65 H), 2.73 (s, sharp, unintegrated), 2.71 (s, sharp, unintegrated), 2.19 (s, sharp, unintegrated), 2.08 (s, sharp, unintegrated). UV-visible (MeCN) $\lambda_{max} = 583$ nm. The unintegrated resonances were extremely minor compared to the other features, so were not included in the integration.

C. Results and Discussion

Chromium

Metal-metal bonds are scarce among the first row transition elements due to the relatively "hard" nature of these metals and the contracted orbital size. Cr(II) is the only element among this group to form dinuclear coordination compounds containing metal-metal bonds. These examples are primarily with bridging ligands such as carboxylate and amidinate ligands to hydroxypyridine anions.¹³ Among these examples are found the extremely short quadruple bonds known as chromium "super shorts." Much discussion about the factors influencing these short distances has been put forth,¹³ and we rationalize that the preparation of unbridged systems if possible, would assist in identifying some of the factors that influence Cr-Cr bonds.

Although this particular dimetal unit seems extremely unlikely to be stabilized by solvent with a high charge which would further serve to contract the orbitals, we decided that this was the only possibility for a dinuclear solvated system among the first row elements, so we targeted " $[Cr_2(MeCN)_{10}]^{4+}$ " to be synthesized by our established methods. Our earliest successful efforts in dirhodium chemistry focused on the decarboxylation reactions with Et₃OBF₄; thus we used this reagent on Cr₂(OAc)₄, in hopes of retaining the M-M bond while several bridging groups were removed. Anhydrous chromium acetate does not possess axial solvent ligands. Instead, the oxygen atoms on one acetate ligate the equatorial site of one Cr_2 unit as well as the axial position of another Cr_2 unit thereby setting up an extended network as presented in Figure 34. Disrupting this network is not particularly difficult- it involves merely dissolution in a coordinating solvent to produce discrete dinuclear units. This reactive form exists in

Figure 34. View of the discrete $Cr_2(OAc)_4L_2$ molecule and the extended interaction in the anhydrous form. (Ref 13)





Figure 34

MeCN, therefore decarboxylation with the reagent Et_3OBF_4 proceeds easily to form a purple solution from which peach crystals may be grown.

X-ray crystallography on the pale orange crystals carried out by Siemens indicated that the compound was actually the previously reported but uncrystallized mononuclear solvated species, $[Cr(MeCN)_6][BF_4]_3$.¹⁴ Preliminary data clearly showed the molecule as presented in Figure 35. Selected bond distances and angles are found in Tables 18 and 19. Positional parameters are located in the Appendix. The chromium atom is ligated by six MeCN ligands in a perfectly octahedral disposition about the metal. Three $[BF_4]$ ⁻ counterions in the lattice indicate that an oxidation from Cr(II) to Cr(III) has occurred during the course of the reaction. This is not particularly surprising, given the extreme sensitivity of the starting material and the established preference for a solvated complex of this oxidation state.¹⁴ Excessive air exposure of this sensitive compound invariably produces green solids and solutions. Evidently, the dinuclear $[Cr_2]^{4+}$ species is far too unstable and the reaction proceeds to form the thermodynamically more stable Cr(III) solvate.

Although there have been previous reports of the homoleptic MeCN Cr^{3+} complex,¹⁴ characterization in each case was limited to electronic spectroscopy and elemental analysis. We were able to detail the solid state properties of $[Cr(MeCN)_6][BF_4]_3$. The ¹H NMR spectrum indicated the presence of free acetonitrile ligands with the usual resonance at $\delta = 1.95$ ppm. This is anticipated both because the ion is d³ and should possess no inherent inhibition to solvent self-exchange, and because a coordinated nitrile signal would be relaxed due to the compound's paramagnetism, even if exchange was incomplete. The FT-IR spectrum of $[Cr(MeCN)_6][BF_4]_3$ displayed two intense stretches in the C=N region at 2330 and 2301 cm⁻¹ due

Figure 35. Diagram of the crystallographically characterized $[Cr(MeCN)_6]^{3+}$.



Figure 35

atom 1	atom 2	distance	atom 1	atom 2	distance
Cr1	N1	1.97 (2)	B1	F1A	1.39(2)
Cr1	N2	1.97(1)	B1	F1B	1.33(2)
Cr1	N3	2.00(1)	B1	F1C	1.35(2)
Cr1	N4	2.01(1)	B1	F1D	1.27(2)
Cr1	N5	1.995(6)	B 2	F2A	1.35(1)
Cr1	N 6	1.990(7)	B 2	F2B	1.35(2)
N1	C1A	1.08(2)	B2	F2C	1.36(1)
N2	C2A	1.12(2)	B 2	F2D	1.38(2)
N3	СЗА	1.14(2)	B3	F3A	1.36(2)
N4	C4A	1.15(2)	B 3	F3B	1.34(2)
N5	C5A	1.11(1)	B 3	F3C	1.35(2)
N6	C6A	1.13(1)	B 3	F3D	1.36(2)
C1A	C1B	1.53(3)			
C2A	C2B	1.53(3)			
C3A	C3B	1.41(2)			
C4A	C4B	1.41(2)			
C5A	C5B	1.48(1)			
C6A	C6B	1.45(1)			

.

Table 18. Selected Bond Distances in Å for [Cr(MeCN)₆][BF₄]₃

atom1	atom2	atom3	angle
N1	Cr1	N2	179.7(5)
N1	Cr1	N3	90.2(5)
N1	Cr1	N4	90.3(6)
N1	Cr1	N5	90.0(6)
N1	Cr1	N6	87.3(6)
N2	Cr1	N3	90.1(5)
N2	Cr1	N4	89.4(5)
N2	Cr1	N5	89.8(6)
N2	Cr1	N6	92.9(5)
N 3	Cr1	N4	177.9(5)
N3	Cr1	N5	89.3(5)
N3	Cr1	N6	89.7(5)
N4	Cr1	N5	88.6(5)
N4	Cr1	N6	92.4(5)
N5	Cr1	N6	177.1(6)
Cr1	N1	C1A	169 (2)
Cr1	N2	C2A	169(1)
Cr1	N 3	C3A	171(1)
Cr1	N4	C4A	173(1)
Cr1	N5	C5A	176(2)
Crl	N6	C6A	171(1)
N1	C1A	C1B	177(2)
N2	C2A	C2B	175(2)
N3	C3A	C3B	175(2)
N4	C4A	C4B	176(2)
N5	C5A	C5B	179 (1)
N6	C6A	C6B	180(2)

Table 19. Selected Bond Angles in degrees for $[Cr(MeCN)_6][BF_4]_3$

to the v(C=N) stretch and the combination CH₃ deformation/C-C stretch. The expected broad $[BF_4]^-$ stretch appeared at 1030 cm⁻¹. Several additional intense features were observed at 959, 470, and 445 cm⁻¹, of which the first can be identified as the C-C stretch by comparison to the extensive Groeneveld literature.¹⁵ The other two features are higher than the reported values for both the C-C=N bend and M-N stretch in divalent octahedral solvates, so these remain unassigned in the absence of a database of infrared spectra of trivalent acetonitrile compounds with which these values may be compared.

Iridium

In contrast to rhodium chemistry, only one dinuclear iridium (II,II) complex has been reported.¹⁶ Diiridium tetracarboxlyates are not known; neither are the octahalide supported metal-metal bonds for the late transition metals with the exception of osmium,¹³ thus available starting materials for accessing the $Ir_2(II,II)$ core are few. Since the acetonitrile solvated Ir(III) complex is also unknown, we proposed to approach through an alternative method. We planned to first prepare $[Ir(MeCN)_6]^{3+}$, and then reduce the cation to Ir(II) which is d⁷ and should have a proclivity to form a metal-metal bond. We argue that the charge on the metals may even improve the stability of the diiridium solvate since this may help to stabilize the lower oxidation state Ir(II) over Ir(III). An encouraging factor for the hypothesized success in the use of acetonitrile to stabilize this M-M bond is that the only known $Ir_2(II,II)$ species is ligated by N-donors rather than the ubiquitous O-donor ligands.¹⁶

Efforts to prepare the Ir^{3+} solvated complex followed much the same course as the halide abstraction reactions with RhCl₃. The IrCl₃ polymeric

network is more robust than that of Rh, so refluxing MeOH was required to prepare a reactive form of the Ir(III) starting material. Acetonitrile was not sufficient to render the material soluble, therefore methanol was required in order to observe any reaction. Reactions of IrCl₃ with SbCl₅ did not seem to proceed cleanly, judging by the large amounts of brown solid that continuously precipitated upon work-up.

Halide abstraction using silver reagents was much more productive, although these reactions proved to suffered from the same impurity problems as the rhodium analogs. The contaminated solids decomposed in light due to the photosensitivity of the Ag^+ impurities. The presence of Ag^+ impurities was also verified by cyclic voltammetry where a catalytic reaction with the electrode occurred at +0.26 V, and by the deterioration of CsI windows during IR studies as the Ag^+ reacted with the salt plates.

The presence of these impurities should not affect qualitative spectroscopic results substantially since the silver salts will be silent in the NMR and IR. The ¹H NMR spectra displayed two resonances, one presumably due to coordinated MeCN at $\delta = 2.82$ ppm, and one of various intensity due to exchanged solvent at $\delta = 1.95$ ppm. The relative intensities of these two features varies with the time elapsed between sample preparation and data collection. The observation of the coordinated ligand is due to the relatively inert nature of the d⁶ Ir(III) metal center; solvent selfexchange is not facile at room temperature.¹⁷ The coordinated solvent resonance is near that of [RhCl₂(MeCN)₄]⁺ and the slight shift may merely reflect the change in metal center. The IR spectrum in the v(C=N) region is also quite similar to that of [RhCl₂(MeCN)₄]⁺, suggesting that the compound that is admixed with the silver impurities may be [IrCl₂(MeCN)₄]⁺ which is unknown. Separation of the iridium and silver containing salts was not

possible due to the extremely similar solubilities of the components. Even multiple fractional recrystallizations were not successful at producing a pure compound.

Efforts to bypass these purity problems involved the use of HBF₄ to remove the halides from IrCl₃. Unfortunately, dry products could not be isolated from these reactions which displayed a distinct tendency to oil. The cyclic voltammetry on a sticky residue displayed complicated behavior of several irreversible reductions at $E_{p,c} = -0.88$ V, -1.05 V, and -1.55 V. No oxidations were observed out to the solvent limit of +2.0V. A typical voltammogram in 0.1 <u>M</u> TBABF₄/MeCN with a glassy carbon working electrode and a Ag/AgCl reference electrode is shown in Figure 36.

Ruthenium

Preparing a dinuclear ruthenium compound presented several new challenges. The first is the choice of oxidation state. The majority of Ru-Ru bonds are mixed-valence II-III complexes; fewer examples of II-II and III-III species exist.¹³ The demonstrated stability of $[Ru(MeCN)_6]^{2+}$ prevents any consideration of forming a dinuclear II,II species, therefore efforts centered on the +3 and mixed valence starting materials. Our initial approach involved halide abstraction from the RuCl₃ starting material since no dinuclear octahalide of this metal is known. Several possible results of these reactions were considered; the previously unknown mononuclear 3+ solvated species could result, or adventitious reduction of half of the ruthenium and dimerization to form a mixed valence complex was proposed.

The first strategy was to remove the halides via reaction of RuCl₃ with a thallium or silver reagent to precipitate the chloride. These reactions produced bright blue solutions. The solids isolated from the AgBF₄ reactions

Figure 36. Cyclic voltammetry of a halide abstraction product with IrCl₃ containing significant Ag⁺ impurity





were thoroughly characterized spectroscopically. The FT-IR spectrum displays two weak features in the v(C=N) region at 2334 and 2305 cm⁻¹. The low intensity of these stretches is not unexpected for a weakly back-bonding Ru(III) compound as discussed in the Introduction of this dissertation. A large [BF₄]⁻ stretch is present with no substantial v(Ru-Cl) stretches in the far-infrared region. The intense blue color of the solutions is reflected by the absorption in the visible region at $\lambda_{max} = 579$ nm which is accompanied by two distinct features in the ultraviolet at maxima of 319 and 267 nm. The ¹H NMR spectrum displays only one resonance at $\delta = 2.49$ ppm which is attributable to coordinated CH₃CN.

All of the aforementioned data support the formulation of a fully solvated species, except the reactions in acidic media to protonate the chlorides from RuCl₃ which do not give solutions that in any way resemble these colors. It seems reasonable to assume therefore, that silver has become incorporated into the product since it will not be detected by any of the aforementioned methods. Protonation reactions of RuCl₃ with HBF₄ produce dark red solutions, but isolation of red products without further transformation was not possible. It is important to note that all the above reactions must be carried out using hydrated starting materials. The anhydrous form proves to be totally unreactive even under prolonged refluxing conditions.

After these halide abstraction reactions had not successfully produced an isolated solvated ruthenium system, additional information about the purity and composition of RuCl₃ starting materials came to light.¹⁸ The solids that are commercially available are purified either for the Ru(III) oxidation state in which case large amounts of HCl contaminate the samples, or if the HCl is removed, the solid contains a mixture of Ru oxidation states.

Neither situation lends itself well to designed syntheses from this material. Thus most Ru reactions are carried out on derivatives whose preparation does not rest on the purity of the RuCl₃.

The first reaction attempted for this metal was decarboxylation of $\operatorname{Ru}_2(O_2CC_2H_5)_4Cl_2$ with Et_3OBF_4 in MeCN, carried out by K.R. Dunbar.¹⁹ These conditions did not proceed to remove the carboxylates as evidenced by a crystal structure of the only product isolated from the reaction which turned out to be the axial aquo adduct of the original species. Although the solvated bis-carboxylate complex, $\operatorname{Rh}_2(OAc)_2(\operatorname{MeCN})_6^{4+}$ does not exist, a derivative of this system possessing four equatorial CO groups is known, and it was hoped that this might change the solubility and open up the unit for reactivity. A reaction was carried out with $\operatorname{Ru}_2(OAc)_2(\operatorname{CO})_4(\operatorname{MeCN})_2$ and Et_3OBF_4 , and while a color change did occur from yellow to orange, the subsequent product proved to be intractable.

Acid reactions with the mixed-valence tetraacetate of ruthenium, with or without the axial halide, appear to proceed more rapidly and completely than the corresponding reactions with Et₃OBF₄, which does not easily attack the relatively insoluble starting material. Red solutions result from the reaction with either HBF₄ or HTFMS, leaving behind only a small amount of unreacted starting material. As in the acidic reactions with RuCl₃, no red product can be isolated from these reactions; the only recognizable component is the pale cation [Ru(MeCN)₆]²⁺ which is apparently a thermodynamic sink for these reactions and is likely to be formed from most mixed valence starting materials. The appearance of this product was seen regardless of whether or not the axial halides were removed prior to acidification.

Molybdenum

The dimolybdenum acetonitrile solvated species, $[Mo_2(MeCN)_{10}]^{4+}$, was the first example of a readily prepared dinuclear MeCN species and is generally accessed directly or indirectly from the tetracarboxlyate dimetal complex.²⁰ As mentioned earlier, $[Re_2(MeCN)_{10}]^{4+}$ may be prepared either from the tetrabutyrate or from the octahalide. We wished to further generalize our methodology to include the preparation of the Mo_2^{4+} species by halide abstraction from $[Mo_2Cl_8]^4$ as well.

Unlike the $[\text{Re}_2\text{Cl}_8]^2$ case, these reactions did not produce the bright blue solutions of the well-known fully solvated dimolybdenum complex. One problem was quite obviously the acidic conditions in which most of these reactions were performed. If the HBF₄ or HTFMS are not perfectly dry, the reaction solutions lead to intractable oils. The green colors resulting from most of the reactions suggest that protonation ceases at the partially solvated compound, Mo₂Cl₄(MeCN)₄. Starting material purity may be affecting the formation of this intermediate compound since the preparation of both K₄[Mo₂Cl₈] and [NH₄]₅[Mo₂Cl₉] are prone to contamination by KCl and NH₄Cl respectively. The presence of additional Cl⁻ would certainly retard the progress of the reaction. The one difficulty with this hypothesis is that the same reaction conditions were employed with Mo₂Cl₄(Me₂S)₄ but these also gave green solutions, although there were only four halides to be removed.

One reaction that was promising in the $[Mo_2]^{4+}$ chemistry was the reaction of K₄[Mo₂Cl₈] with NaBPh₄. The room temperature reaction produced a blue solution that unfortunately decomposed to a green solution upon accidental exposure to air, but this sensitivity is typical of the target complex, $[Mo_2(MeCN)_{10}]^{4+}$. More careful treatment of this reaction or possible use of silver reagents may assist the preparation of the solvated

cation from this halide route. At this point, a great deal of effort has not been expended on this reaction since the dinuclear solvate of molybdenum is already known.

Osmium

In contrast to ruthenium, there are no homoleptic acetonitrile species, either mononuclear or dinuclear, known for osmium. As a third row metal, higher oxidation states are more stable so the common carboxylate is $Os_2(III,III)$ instead of the mixed valence $Ru_2(II,III)$ system.¹³ This would necessitate the initial formation of a solvated Os compound with an $[Os_2]^{6+}$ core, but as seen for rhenium, another third row element, a reduction was observed from $Re_2(III,III)$ to $Re_2(II,II)$, therefore, it would not be surprising if $[Os_2]^{4+}$ was the more stable dinuclear solvated molecule.

The halide abstraction reactions with $OsCl_3$ produced similar results as the RuCl₃ chemistry. The inky blue solutions gave sticky solids upon which no characterization was obtained. This reaction was not followed up due to a lack of a convenient source of $OsCl_3$. We had received a large quantity of OsO_4 from Johnson -Matthey and decided that the dinuclear starting materials $[n-Bu_4N]_2[Os_2Cl_8]$ and $Os_2(OAc)_4Cl_2$, prepared from OsO_4 , would be even better starting materials for the fully solvated systems.

Halide abstraction reactions with the green $[Os_2Cl_8]^{2}$ generated brown solutions. The three reagents employed, AgTFMS, HBF4, and HTFMS all produced slightly different results. The lack of white precipitate in the silver reaction combined with the very weak nitrile stretches in the infrared and persistence of substantial $[n-Bu_4N]^+$ in the ¹H NMR spectrum suggested that this product was not the desired fully-solvated species. The acidic reactions did not produce solids and displayed a marked propensity towards oiling. The combination of propionitrile and triflic acid in particular is less likely to produce a solid owing to the enhanced solubility of both the triflate anion and the longer chain nitrile.

Considering the difficulties encountered in the attempted synthesis of $[Mo_2(MeCN)_{10}]^{4+}$ from the dinuclear halide, more attention was focused on $Os_2(OAc)_4Cl_2$ than on $[Os_2Cl_8]^2$. Early reactivity surveys indicated that the insolubility of the starting material precluded reaction with Et_3OBF_4 .¹⁹ Indeed, most reactions employing osmium tetracarboxylates as starting materials are generally carried out with a longer chain R-groups to enhance the solubility.¹² Thus it is quite surprising that the brown insoluble $Os_2(OAc)_4Cl_2$ reacts with HBF₄ in MeCN to produce a green solution. Unfortunately, preliminary efforts to isolate a solid from this tantalizing solution proved fruitless, but this reaction is very promising and should be pursued. The combination of a silver reagent to remove the axial chlorides followed by Me₃SiTFMS to remove the carboxylates was adopted from the demonstrated success of a two-step method in the rhenium chemistry; nevertheless, a lack of nitrile stretches in the infrared suggested that this was not a viable method.

In the first reaction that we used to produce $[Rh_2(MeCN)_{10}][BF_4]_4$, the triethyloxonium reagent was introduced as a CH_2Cl_2 solution, the presence of which served to precipitate the product from the MeCN reaction solution. This strategy was also tried in the osmium chemistry. Addition of CH_2Cl_2 to the MeCN reaction solutions does not precipitate a green product, but instead causes the reaction to turn color, in this case purple. Two compounds were isolated from this reaction, the principal products are a dark blue species and a bright purple compound. Neither compound displays v(Os-Cl) stretches down to 200 cm⁻¹ in the infrared, but both contain carboxylate stretches

around 1550 cm^{-1} with the feature in the blue sample more prominent than that of the purple. The purple spectrum displays only one v(C=N) stretch at 2294 cm^{-1} compared to the blue compound which displays both a stretch at 2298 and an additional feature at 2330 cm^{-1} . The ¹H NMR of the blue compound displays several very broad resonances shifted downfield to $\delta =$ 12.2 and 9.8 ppm suggesting the presence of a paramagnetic component which contact shifts these signals. The intense blue color also implicates a mixed valence species. Thus, it is anticipated that the blue species is partially reduced to Os_2^{5+} and is ligated by a mixture of acetate and acetonitrile. The ¹H NMR spectrum of the purple compound displays several singlets at $\delta = 8.58, 6.07, 2.71, 2.19$ and 2.08 ppm. The sharp nature of the resonances indicates a diamagnetic compound which presumably is ligated by OAc⁻ and MeCN. A methodical approach to separation of these two compounds is necessary before more emphasis is placed on spectral identification. Crystallization of the two species would greatly assist in understanding the influence of the CH_2Cl_2 and assessing the next step in successfully accessing a fully solvated complex.

D. Summary

Several mononuclear compounds resulted from attempts to prepare dinuclear solvated species. The chromium system proved the efficacy of triethyloxonium reagents in producing solvated compounds, even if the $[Cr(MeCN)_6]^{3+}$ species was not what we had initially attempted to prepare. Efforts to access $[Ir(MeCN)_6]^{3+}$ as a precursor to an $[Ir_2(MeCN)_{10}]^{4+}$ compound were met with lability problems in the $IrCl_3$ system. Future investigations would benefit from slightly different strategies. One possibility is the use of $IrBr_3$ instead of the chlorides since the larger, more polarizable halides should be easier to remove. Another possibility would be to prepare one of the examples of an assembled $Ir_2(II,II)$ core and try to protonate the ligands in the presence of acetonitrile. The dehydration of $[Ir(H_2O)_6]^{3+}$ has been discussed as an option, but the difficulty of completely removing all the water coupled with the extreme substitutional inertness of this complex makes this method more attractive.¹⁷

Synthesis of any solvated Ru complex other than $[Ru(MeCN)_6]^{2+}$ seems unlikely at this point considering both the thermodynamic stability of that compound and the impurities contained in the only convenient starting material, RuCl₃. Continuation of this work should receive a low priority, although elucidation of the inky blue solutions resulting from the halide abstraction reactions with Ag⁺ reagents are quite intriguing. Likewise, the $[Mo_2]^{4+}$ chemistry is not as important to generalize as that of the other metals since the fully solvated compound is already known.

Of the metal systems discussed, $[Os_2]^{4+}$ has shown the most promise thus far. The dark blue and purple compounds resulting from the reactions involving the addition of CH_2Cl_2 may not be fully solvated complexes, but they definitely present more soluble forms of the acetate starting material from which it may be easier to finally prepare the sought after $[Os_2(MeCN)_{10}]^{n+}$. The ease of isolating dry solids of these compounds is also extremely promising. Alternately, rigorously anhydrous conditions may allow isolation of a solid from the oily acid solutions. Addition of the acid anhydride should also assist in this process.

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CHAPTER VI

CONCLUDING REMARKS AND FUTURE DIRECTIONS

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General

The chemistry of partially and fully solvated transition metal cations was largely unexplored prior to the results in this dissertation. The versatile combination of a positively charged dinuclear core and labile ligands may be exploited in designing new molecules that are inaccessible through more common starting materials; future applications such as incorporation of dimetal units into porphyrins and materials would be attractive future directions. The small number of dinuclear solvated complexes prompted our investigation into establishing general methods of preparing other examples and to study the fundamental reactivity of these species.

Mixed-Metal Cation-Anion reactions

The partially solvated dirhodium cation $[Rh_2(OAc)_2(MeCN)_6]^{2+}$ reacts with the anionic $[Re_2Cl_8]^{2-}$ to yield the unusual soft salt, $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$. The partially solvated molybdenum dication does not produce the same kinetic product as the rhodium analog, so the elucidation of a thermodynamic product in this second system will probably lend more insight into the identification of redissolution products of $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$ in MeCN. The reactions of transition metal cations and anions have generally not been extensively investigated and are rich with potential for ligand redistribution, clusterification through cationanion annihilation, preparation of unusual mixed-metal salts, or possible use as molecular precursors for materials.

Synthesis and Reactivity of Dirhodium Solvates

Several methods for preparing solvated dinuclear transition metal cations have been elucidated. The use of triethyloxonium tetrafluoroborate

as a carboxylate alkylation agent was the first method that led to clean preparation of the solvated species $[Rh_2(MeCN)_{10}][BF_4]_4$. Acidification of the carboxylates with tetrafluoroboric acid was also found to be an excellent route to prepare this nitrile cation in high yield. Preparation of a more soluble salt was also established through the silylation reaction of dirhodium tetraacetate with trimethylsilyltriflate. Solvent exchange on the acetonitrile compound is quite facile for both the axial and equatorial positions as observed by ¹H NMR. This characteristic allows the substitution of water for MeCN to prepare the elusive $Rh_2(aq)^{4+}$ in a non-acidic medium. The synthesis of homoleptic dirhodium cations with different solvents and counterions allows for the use of these synthons in specifically reactions.

Photochemistry of [Rh₂(MeCN)₁₀]⁴⁺

The photochemistry of the dirhodium decakisacetonitrile complex is fascinating due both the reversibility and to the half-life of the process. That this process occurs under normal synthetic conditions has been established by examining the electronic spectra of samples exposed to ambient light or refluxing conditions in the absence of light. Although independent synthesis of the intermediates has not been possible to this point, verification of the Rh(I) and Rh(III) intermediates was established by trapping the Rh(I) intermediate by purging a photolyzed solution of $[Rh_2(MeCN)_{10}][BF_4]_4$ with CO gas to obtain cis- $[Rh(CO)_2(MeCN)_2]^+$.

Other Transition Metal Systems

Extrapolation of the synthetic methods to access $[Rh_2(MeCN)_{10}]^{4+}$ to other transition metals was met with mixed success. Attempts to work with chromium tetraacetate lead to an oxidation to form the stable mononuclear

 $[Cr(MeCN)_6]^{3+}$ species. Ruthenium is problematic because RuCl₃ is an impure starting material and a thermodynamic sink for the reactions is the mononuclear species, $[Ru(MeCN)_6]^{2+}$. Preparation of a diiridium complex will necessarily be more complicated than dirhodium due to a paucity of appropriate starting materials and the inertness of IrCl₃. Halide abstraction from IrBr₃ and subsequent reduction, or protonation of the ligands on the $Ir_2(form)_4(II,II)$ (form = formamidinate) complex should definitely be investigated. Attempts to access the diosmium system have discovered a surprisingly rich chemistry from the reactions of $Os_2(OAc)_4Cl_2$; this is currently the most promising metal for future work.

General accessibility to solvated systems was established in both dirhodium and dirhenium chemistry through the use of trialkyloxonium reagents and acids. The osmium system, however, demonstrated that Et₃OBF₄ is not as forcing a reagent as either tetrafluoroboric acid or trifluoromethanesulfonic acid since $Os_2(OAc)_4 Cl_2$ does not react in the presence of triethyloxonium. The difficulties with the acidic media are the complications encountered in isolating the products. Several suggestions are proposed to alleviate these difficulties. The first is the addition of both the acid and the acid anhydride to the reaction which should help to scavenge the water. The second requires distillation of all reagents involved prior to combination. A third possibility involves the use of a specialized piece of glassware designed specifically for this purpose, depicted in Figure 37. This combination condenser/ water trap allows the reaction to be refluxed as the solvent is distilled through molecular sieves which should dehydrate the solution. The efficacy of this process has already been demonstrated for organic reactions.¹ and extrapolation to inorganic reactions should also prove very effective. Some difficulty may be encountered since MeCN refluxes at a

Figure 37. Diagram of a condenser and water trap to dehydrate reaction solutions

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Figure 37

lower temperature than H_2O , but the substitution of higher boiling nitriles should alleviate this problem.

Conclusions

Preparation of a fully solvated dirhodium cation has been established for two different nitriles with two different anions, and the fundamental reactivity of these complexes with the aim of designed synthesis has been established. Decakisacetonitrile dirhodium itself exhibits unusual reactivity in the form of reversible photochemistry. Synthetic exploration of other related transition metal compounds has provided useful insight into the future selection of the most likely metals to form these dimetal solvates and which particular starting materials will most likely produce the best results. This research has effectively laid the ground work for establishing general routes into homoleptic acetonitrile dinuclear transition metal species.

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APPENDICES

Synthetic Methods

All experiments were carried out using standard vacuum and Schlenk line techniques unless otherwise noted. Starting materials were obtained from commercial sources where no other source is indicated. All nitriles except for acetonitrile were used as received. MeCN, MeOH, diethyl ether, hexanes, toluene, THF, CH₂Cl₂, and acetone were distilled under N₂ from an appropriate drying agent prior to use. Water was purified by the Millipore system from Waters Chromatography and was deoxygenated by a purge of inert gas.

Physical Measurements

Infrared spectra were measured on either a Nicolet 740 FT-IR or a Perkin-Elmer 599 Spectrophotometer. ¹H NMR experiments were performed on a Varian Gemini 300 MHz instrument. Electronic Spectroscopy was carried out on a Hitachi U-2000, a Cary 17, or a Cary 2300 spectrophotometer in the indicated solvents in quartz cells. Electrochemical measurements were carried out using an EG&G Princeton Applied Research Model 352 scanning potentiostat in conjunction with a BAS Model RXY recorder and were uncorrected for junction potentials. Platinum working electrodes were used with potentials referenced to a Ag/AgCl reference electrode an internal Ferrocene standard was not used. EPR experiments were carried out on a Varian E-4 spectrometer at room temperature. Elemental Analyses were performed by either Galbraith Laboratories, or Desert Analytics. Table 20. Atomic Positional Parameters $(Å^2)$ and their estimated standard deviations for $[Rh_2(OAc)_2(MeCN)_6][Re_2Cl_8]$

atom	x	У	2	B(eq)
atom Re(1) Cl(1) Cl(2) Cl(3) Cl(4) Re(2) Re(3) Cl(5) Cl(6) Cl(6) Cl(6) Cl(6) Cl(6) Cl(6) Cl(6) Cl(6) Cl(6) Cl(6) Cl(10) Cl(11) Cl(12) Cl(12) Cl(13) Cl(14) Cl(15) Cl(16) Rh(1) Rh(2) O(1) O(2) O(3) Cl(2) Cl(3) Cl(2) Cl(3) Cl(2) Cl(3) Cl(2) Cl(3) Cl(2) Cl(3) Cl(3) Cl(4) Re(3) Cl(5) Cl(6) Cl(10) Cl(10) Cl(10) Cl(11) Cl(11) Cl(12) Cl(11) Cl(12) Cl(10) Cl(11) Cl(12) Cl(11) Cl(12) Cl(11) Cl(12	x 0.72337(7) 0.7105(5) 0.7720(5) 0.7078(5) 0.6478(4) 1/4 1/4 0.2323(4) 0.1698(4) 0.3319(4) 0.2496(5) 0.48111(8) 0.55419(8) 0.55419(8) 0.5559(3) 0.5184(5) 0.6035(4) 0.5612(4) 0.5612(4) 0.4312(5) 0.4312(5) 0.4312(5) 0.4326(4) 0.5401(5) 0.4781(1) 0.550(1) 0.533(1) 0.4528(8)	y 0.21857(7) 0.2006(5) 0.1495(4) 0.2032(5) 0.2577(5) 1/4 1/4 0.3318(4) 0.2323(4) 0.2323(4) 0.2503(4) 0.3343(4) 0.03067(9) 0.02364(8) 0.0626(4) 0.0626(4) 0.0963(4) 0.0626(4) 0.0963(4) 0.0626(4) 0.0963(4) 0.0626(4) 0.0963(4) 0.072(5) -0.0523(4) 0.0708(5) 0.1064(5) -0.0183(5) 0.2297(1) 0.2295(1) 0.3188(8) 0.2595(8)	z 0.7398(1) 0.6167(6) 0.7417(6) 0.8640(5) 0.7371(7) 0.4412(1) 0.3191(1) 0.4718(5) 0.4723(5) 0.2906(5) 0.2885(5) 0.2817(1) 0.2312(1) 0.2312(1) 0.2312(1) 0.2312(1) 0.2349(6) 0.3204(5) 0.3204(5) 0.3462(7) 0.1956(6) 0.3914(6) 0.2389(6) 0.2389(6) 0.1207(7) 0.1173(2) 0.0052(2) -0.012(1) 0.111(1)	B(eq) 2.67(8) 3.9(6) 3.7(6) 3.8(6) 4.3(6) 1.7(1) 1.6(1) 2.4(5) 2.2(5) 2.6(5) 2.7(5) 2.1(1) 1.87(9) 2.2(4) 4.0(5) 2.7(5) 2.6(5) 5.4(7) 4.8(7) 4.8(7) 4.8(7) 4.8(7) 1.7(1) 1.8(1) 1.5(5) 2(1) 0.7(4)
D(3) D(4) N(1) N(2) N(3) N(4) N(5)	0.4578(8) 0.442(1) 0.483(1) 0.576(1) 0.545(1) 0.423(1) 0.516(1)	0.2585(8) 0.311(1) 0.164(1) 0.206(1) 0.201(1) 0.222(1) 0.231(1)	$-0.048(1) \\ 0.042(2) \\ 0.019(2) \\ 0.050(2) \\ -0.101(2) \\ 0.125(1) \\ 0.192(1) \\ 0.212(2)$	0.7(4) 3(1) 2.2(7) 2.0(7) 2.3(7) 1.5(6) 0.7(5) 2.2(7)
C(1) C(2) C(3) C(4) C(5) C(6) C(7)	0.554(1) 0.585(2) 0.434(2) 0.405(2) 0.471(2) 0.450(1) 0.615(2)	0.327(1) 0.369(2) 0.296(2) 0.326(2) 0.125(2) 0.074(1) 0.192(2)	0.048(2) 0.036(2) -0.029(2) -0.070(2) 0.031(2) 0.049(2) 0.063(3)	1.4(7) 3(1) 2.0(8) 2.9(9) 2.2(8) 1.0(6) 3(2)
C(8) C(9) C(10) C(11) C(12) C(12) C(13) C(14) C(15)	0.666(2) 0.550(2) 0.564(2) 0.390(1) 0.344(2) 0.528(1) 0.548(2) 0.434(1)	0.176(2) 0.179(2) 0.150(2) 0.198(1) 0.163(2) 0.210(1) 0.183(2) 0.324(1)	0.081(3) -0.154(2) -0.225(2) 0.135(2) 0.144(2) 0.241(2) 0.303(2) 0.265(2)	5(1) 2(2) 3(1) 1.9(7) 4(1) 2.0(8) 3(1) 2.1(8)

Table 20. continued

atom	x	У	2	B(eq)
C(16) Rh(3) Rh(4) O(5) O(6) O(7) O(8) N(7) N(8) N(9) N(10) N(11) N(12) C(17) C(18) C(17) C(18) C(17) C(18) C(20) C(21) C(22) C(22) C(23) C(24) C(25) C(26) C(27) C(28) C(29) C(30) C(31)	0.416(2) 0.2304(1) 0.2662(1) 0.2396(8) 0.1881(8) 0.1801(8) 0.201(1) 0.290(1) 0.292(1) 0.277(1) 0.277(1) 0.190(1) 0.201(2) 0.175(1) 0.175(1) 0.173(1) 0.126(2) 0.303(2) 0.327(2) 0.327(2) 0.327(2) 0.327(2) 0.314(2) 0.340(1) 0.294(2) 0.302(1) 0.337(1) 0.179(2)	0.341(2) 0.4810(1) 0.5229(1) 0.462(1) 0.4458(8) 0.5356(8) 0.554(1) 0.582(1) 0.492(1) 0.554(1) 0.554(1) 0.514(1) 0.425(1) 0.443(2) 0.443(2) 0.443(2) 0.443(2) 0.557(1) 0.588(2) 0.620(2) 0.672(2) 0.672(2) 0.672(2) 0.672(2) 0.588(2) 0.567(2) 0.583(2) 0.526(2) 0.538(2) 0.392(1) 0.347(1) 0.440(2)	$\begin{array}{c} 0.342(2)\\ 0.1234(2)\\ 0.0127(1)\\ -0.047(1)\\ 0.048(1)\\ 0.118(1)\\ 0.007(1)\\ 0.058(2)\\ 0.022(2)\\ -0.094(2)\\ 0.200(2)\\ 0.127(1)\\ 0.218(2)\\ -0.016(2)\\ -0.016(2)\\ -0.071(2)\\ 0.057(2)\\ 0.057(2)\\ 0.052(3)\\ 0.073(2)\\ 0.034(2)\\ 0.034(2)\\ 0.040(2)\\ -0.145(2)\\ -0.213(2)\\ 0.254(2)\\ 0.320(2)\\ 0.131(2)\\ 0.136(2)\\ 0.274(2)\\ \end{array}$	3(1) 1.6(1) 1.7(1) 2(1) 0.8(4) 0.9(4) 2.4(6) 2.0(6) 1.9(6) 2(2) 0.7(5) 4(2) 3(1) 1.9(8) 1.4(7) 5(1) 3(1) 2.9(9) 3.0(9) 2.5(8) 2.2(7) 2.0(8) 3(1)
C(32)	0.101(1)	0.425(1)	U.342(2)	T•2(1)

Table 21. Atomic Positional Parameters $(Å^2)$ and their estimated
standard deviations for $[Rh_2(MeCN)_{10}][BF_4]_4$

Atom	× -	<u>Y</u>	z -	B(A2)
Rh(1)	0.55984(3)	0.07960(4)	0.30154(2)	2.62(1)
N(1)	0.4161(3)	-0.0754(4)	0.2269(3)	3.0(1)
N(2)	0.4967(3)	0.0160(4)	0.3700(3)	3.1(1)
N(3)	0.5356(3)	0.2340(4)	0.3324(3)	3.3(1)
N(4)	0.6189(3)	0.1460(4)	0.2300(3)	3.3(1)
N(5)	0.6621(4)	0.0783(5)	0.3847(3)	4.2(1)
C(1)	0.9019(4)	0.3349(5)	0.2390(4)	3.2(1)
C(2)	0.3853(6)	-0.2801(6)	0.2586(5)	6.0(2)
C(3)	0.4547(4)	-0.0177(6)	0.4062(3)	3.4(1)
C(4)	0.3989(5)	-0.0589(7)	0.4462(4)	5.0(2)
C(5)	0.5256(4)	0.3217(6)	0.3500(4)	3.6(1)
C(6)	0.5093(5)	0.4379(6)	0.3720(5)	5.4(2)
C(7)	0.6532(4)	0.1895(6)	0.1913(4)	3.4(1)
Atom	× -	<u>У</u>	z -	B(A2)
-------	-----------	------------	-----------	---------
C(8)	0.6963(5)	0.2419(8)	0.1382(4)	5.3(2)
C(9)	0.7221(5)	0.0784(7)	0.4156(5)	5.0(2)
C(10)	0.7979(7)	0.082(1)	0.4542(8)	10.7(5)
B(1)	0.2932(6)	0.4351(8)	0.1907(8)	6.9(3)
F(1)	0.2137(5)	0.0125(6)	0.3592(4)	12.7(3)
F(2)	0.2361(6)	-0.1624(7)	0.3251(6)	16.5(3)
F(3)	0.6380(4)	0.4265(5)	0.2662(4)	9.2(2)
F(4)	0.2499(6)	0.473(1)	0.2405(7)	23.5(4)
B(2)	0.5593(9)	-0.276(1)	0.4579(5)	9.2(4)
F(5)	0.5874(4)	-0.3714(5)	0.4897(3)	8.1(2)
F(6)	0.5536(4)	-0.1953(5)	0.5022(3)	9.7(2)
F(7)	0.5339(6)	-0.2730(7)	0.3879(4)	12.8(3)
F(8)	0.4752(9)	-0.3125(8)	0.4465(8)	20.6(5)

atom	x	У	2	B(eq)
atom Rh(1) Rh(2) N(1) N(2) N(3) N(4) N(5) N(6) N(7) N(8) N(9) N(10) C(1) C(2) C(3) C(4) C(5) C(4) C(5) C(6) C(7) C(2) C(10) C(12) C(12) C(13) C(15) C(16) C(17) C(18) C(19) C(19) C(20) S(2)	x 0.0217(1) 0.1390(1) 0.259(1) 0.208(1) 0.018(1) 0.074(1) 0.022(1) 0.152(1) 0.068(1) -0.110(1) -0.075(1) 0.327(1) 0.327(1) 0.414(1) 0.310(2) -0.052(1) -0.150(1) 0.266(2) 0.302(3) -0.045(1) 0.221(1) 0.316(1) 0.185(2) -0.120(1) -0.179(2) 0.1648(4)	<pre>Y 0.91918(6) 0.98563(6) 0.9864(6) 0.9163(6) 0.9840(6) 1.0587(6) 1.0440(7) 0.8669(6) 0.8676(6) 0.9694(5) 0.9694(5) 0.9718(6) 0.8657(7) 0.9860(7) 0.9820(9) 0.878(1) 0.8262(8) 0.977(1) 1.1008(8) 1.1583(8) 1.086(1) 1.146(1) 0.8355(7) 0.8396(8) 0.7967(8) 0.9978(7) 1.0356(8) 0.8375(7) 0.802(1) 0.6702(3)</pre>	z 0.21053(6) 0.30599(6) 0.2457(6) 0.3555(7) 0.3661(6) 0.2551(7) 0.3818(7) 0.2887(6) 0.2052(6) 0.1342(7) 0.2134(7) 0.2134(7) 0.1309(8) 0.2102(9) 0.157(1) 0.3851(8) 0.422(1) 0.4004(9) 0.443(1) 0.2347(8) 0.207(1) 0.408(1) 0.2447(8) 0.207(1) 0.408(1) 0.408(1) 0.441(1) 0.3288(8) 0.1990(8) 0.192(1) 0.0367(8) 0.2094(8) 0.202(1) 0.085(1) 0.022(1) 0.3059(3)	B(eq) 2.57(5) 2.55(5) 2.6(5) 3.4(6) 3.1(6) 3.2(6) 4.4(8) 3.2(2) 2.7(6) 2.6(6) 3.1(6) 4.3(7) 3.4(8) 4.6(9) 3.9(9) 6(1) 3.7(8) 6(1) 3.1(8) 5(1) 11(2) 3.3(3) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 2.7(7) 3.4(8) 4.6(9) 3.6(1) 3.6(1) 3.1(8) 5(1) 3.6(2) 3.6(2) 3.6(2) 3.6(2) 3.6(2) 3.6(2) 3.6(2) 3.6(2) 3.6(2) 3.6(2) 3.7(8) 6(1) 3.6(2)
O(4) O(5) O(6) S(1) O(1)	0.232(1) 0.151(1) 0.180(1) 0.3236(4) 0.254(1)	0.6670(8) 0.7232(9) 0.6210(7) 1.3704(2) 1.3896(6)	0.247(1) 0.340(1) 0.3517(8) 0.5216(3) 0.4578(7)	10(1) 13(1) 8(1) 5.2(3) 5.6(7) 7 9(8)
O(2) O(3) S(4) O(10) O(11) O(12)	0.433(1) 0.271(1) 0.9300(7) 1.025(2) 0.900(2) 0.947(2)	1.3712(8) 0.1603(4) 0.182(1) 0.222(1) 0.1171(7)	0.5257(8) 0.5884(7) 0.4309(4) 0.386(1) 0.465(1) 0.479(1)	9(1) 10.0(5) 17(2) 13(1) 13(1)
S(3) O(7) O(8) O(9) N(11)	0.4091(6) 0.524(2) 0.380(2) 0.343(2) 0.372(2)	0.1128(3) 0.123(1) 0.056(1) 0.1297(8) 0.052(1)	0.6799(4) 0.686(1) 0.703(1) 0.613(1) 0.950(1)	8.7(4) 16(2) 17(2) 12(1) 11.3(7)
C(25) C(26)	0.425(2) 0.493(2)	0.086(1) 0.134(1)	0.975(1) 1.006(1)	7.4(6) 10.0(8)

Table 22. Atomic Positional Parameters ($Å^2$) and their estimated standard deviations for [Rh₂(MeCN)₁₀][TFMS]₄

Table 22. continued

atom	x	У	Z	B(eq)
C(27)	-0.080(1)	0.7928(8)	0.383(1)	4.9(4)
C(21)	0.3362(7)	1.2924(3)	0.5079(5)	8.9(2)
F(1)	0.2374(6)	1.2688(6)	0.5004(6)	8.9(2)
F(2)	0.3809(9)	1.2848(6)	0.4486(5)	8.9(2)
F(3)	0.3983(8)	1.2673(6)	0.5619(5)	8.9(2)
C(22)	0.0273(8)	0.6590(5)	0.2550(6)	12.6(3)
F(4)	-0.050(1)	0.6577(7)	0.2977(7)	12.6(3)
F(5)	0.008(1)	0.7026(5)	0.2094(8)	12.6(3)
F(6)	0.027(1)	0.6094(5)	0.2194(8)	12.6(3)
C(24)	0.819(1)	0.1486(6)	0.3665(7)	14.9(3)
F(10)	0.732(1)	0.1371(8)	0.3987(9)	14.9(3)
F(11)	0.795(2)	0.1907(6)	0.319(1)	14.9(3)
F(12)	0.848(1)	0.1014(7)	0.333(1)	14.9(3)
C(23)	0.366(1)	0.1660(5)	0.7501(6)	13.6(3)
F(7)	0.392(1)	0.2176(7)	0.7261(9)	13.6(3)
F(8)	0.262(1)	0.1653(8)	0.759(1)	13.6(3)
F(9)	0.427(1)	0.1555(8)	0.8121(9)	13.6(3)

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Table 23.	Atomic Positional Parameters $(Å^2)$ and their estimated
standard	deviations for [Rh ₂ (EtCN) ₁₀][BF ₄] ₄

atom	x	У	Z	B(eq)
Rh(1)	0.05269(2)	0.04196(3)	0.29423(2)	2 .83(2)
F(1)	0.0619(2)	0.1866(3)	0.0230(2)	6.5(2)
F(2)	0.0268(2)	0.2750(4)	-0.0789(3)	7.3(2)
F(3)	0.1294(3)	0.2011(4)	-0.0717(2)	7.8(3)
F(4)	0.1093(2)	0.3423(3)	-0.0041(3)	7.0(2)
F(5)	0.3518(2)	0.1394(4)	0.7383(3)	7.3(2)
F(6)	0.2698(3)	0.2496(5)	0.6949(4)	11.0(4)
F(7)	0.3008(3)	0.1202(7)	0.6253(4)	13.4(5)
F(8)	0.2437(3)	0.0897(7)	0.7234(4)	13.4(5)
N(1)	0.1090(2)	0.1032(3)	0.2185(2)	3.2(2)
N(2)	0.0758(2)	-0.1034(3)	0.2648(2)	3.2(2)
N(3)	-0.0040(2)	-0.0164(3)	0.3700(2)	3.0(2)
N(4)	0.0326(3)	0.1875(4)	0.3275(3)	4.0(2)
N(5)	0.1437(3)	0.0366(4)	0.3640(3)	4.9(3)
C(1)	0.1448(3)	0.1441(4)	0.1821(3)	3.7(2)
C(2)	0.1915(3)	0.1991(6)	0.1365(3)	5.0(3)
C(3)	0.2243(4)	0.1245(6)	0.0826(4)	5.8(4)
C(4)	0.0946(3)	-0.1858(5)	0.2561(4)	5.2(3)
C(5)	0.111(1)	-0.297(1)	0.227(1)	4.5(8)
C(5A)	0.130(1)	-0.291(2)	0.263(1)	6(1)
C(6)	0.1158(9)	-0.370(1)	0.289(1)	6.0(8)
C(6A)	0.079(1)	-0.367(1)	0.228(1)	9(1)
C(7)	-0.0364(3)	-0.0472(4)	0.4146(3)	3.3(2)
C(8)	-0.0778(3)	-0.0830(5)	0.4727(3)	4.0(2)
C(9)	-0.1308(4)	-0.1627(6)	0.4459(4)	6.3(4)

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atom	x	У	z	B(eq)
				_
C(10)	0.0258(4)	0.2683(5)	0.3482(4)	6.4(4)
C(11)	0.000(1)	0.387(1)	0.363(1)	5.0(8)
C(11A)	0.035(1)	0.371(1)	0.397(1)	5.4(9)
C(13)	0.1981(4)	0.0155(8)	0.3814(4)	6.3(4)
C(14)	0.2710(5)	-0.0156(8)	0.4020(6)	7.9(5)
C(15)	0.3016(6)	0.0688(9)	0.4427(6)	9.3(6)
C(12)	0.0448(9)	0.417(1)	0.428(1)	6.3(8)

0.435(2)

0.2525(6)

0.1422(9)

0.359(1)

-0.0337(4)

0.6950(6)

9(1)

4.7(3)

7.1(5)

Table 23. continued

C(12A) -0.020(1)

0.0815(4)

0.2929(5)

B(1)

B(2)

Table 24. Atomic Positional Parameters $(Å^2)$ and their estimated standard deviations for $[RhCl_2(MeCN)_4][BF_4]$

atom	x	У	Z	B(eq)
Rh(l)	0	1/2	0	2.42(3)
Cl(1)	-0.2211(2)	0.3453(1)	0	3.73(6)
N(1)	0.1860(4)	0.4319(2)	0.0671(1)	3.0(1)
C(1)	0.2984(5)	0.3912(3)	0.1024(2)	3.1(1)
C(2)	0.4378(8)	0.3369(4)	0.1496(2)	4.8(2)
B(1)	0	1/2	1/4	3.8(5)
F(2)	-0.1169(6)	0.4343(4)	0.2117(2)	10.4(3)

Table 25. Atomic Positional Parameters $(Å^2)$ and their estimated standard deviations for $[Cr(MeCN)_6][BF_4]_3$

Atom	x	У	Z
Cr1	0.3619	0.0333	0.1780
N1	0.2682	-0.0092	0.0820
C1A	0.2123	-0.0167	0.0301
C1B	0.1306	-0.0316	-0.0398
HIA	0.1484	-0.0846	-0.0863
H1B	0.1175	0.0384	-0.0687
HIC	0.0739	-0.0568	-0.0079
N2	0.4551	0.0762	0.2744
C2A	0.4993	0.1157	0.3307
C2B	0.5622	0.1762	0.4012
H2A	0.5657	0.1326	0.4567
H2B	0.5340	0.2468	0.4153
H2C	0.6259	0.1869	0.3767
N3	0.4554	0.0802	0.0795
C3A	0.5050	0.1212	0.0266
C3B	0.5627	0.1651	-0.0449
H3A	0.6146	0.2058	-0.0171
H3B	0.5240	0.2143	-0.0817
H3C	0.5886	0.1078	-0.0837
N4	0.2669	-0.0079	0.2777
C4A	0.2058	-0.0204	0.3298
C4B	0.1324	-0.0353	0.3963
H4A	0.1274	-0.1097	0.4192
H4B	0.0731	-0.0149	0.3665
H4C	0.1447	0.0140	0.4471
N5	0.3076	0.1862	0.1793
C5A	0.2797	0.2722	0.1757
C5B	0.2447	0.3881	0.1704
H5A	0.2061	0.4092	0.2227
H5B	0.2071	0.3942	0.1147
H5C	0.2998	0.4359	0.1662
N6	0.4131	-0.1203	0.1705
C6A	0.4354	-0.2096	0.1760
C6B	0.4639	-0.3250	0.1827
H6A	0.4815	-0.3540	0.1232
H6B	0.4105	-0.3665	0.2069
H6C	0.5178	-0.3309	0.2241

Table 25. continued

Atom	x	У	Z
B1	0.1998	-0.3268	0.0009
F1A	0.1784	-0.4393	0.0026
F1B	0.1240	-0.2787	0.0410
F1C	0.2060	-0.2906	-0.0875
F1D	0.2805	-0.3064	0.0390
B2	0.5177	0.3787	0.1787
F2A	0.5782	0.466 0	0.1784
F2B	0.4605	0.3776	0.2548
F2C	0.5699	0.2837	0.1736
F2D	0.4599	0.3838	0.1010
B 3	0.3031	0.1647	0.8525
F3A	0.3388	0.0614	0.8681
F3B	0.2199	0.1527	0.8061
F3C	0.3663	0.2288	0.8053
F3D	0.2860	0.2064	0.9384

