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A PROGRESS REPORT SUBMITTED TO THE DEPARTMENT OF ENERGY

FOR SUPPORT OF RESEARCH ENTITLED:

OLIGOMER AND MIXED-METAL COMPOUNDS. POTENTIAL MULTIELECTRON TRANSFER AGENTS

GRANT NO. DE-FG05-84ER13263

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AMOUNT FUNDED:	$303,076 (Three Years)
TIME PERIOD OF REPORT:	January 1, 1987 - January 1, 1990
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Principal Investigator

1/10/90
Date

MASTER

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Significant Accomplishments

We proposed to continue syntheses and characterizations of monometallic and multimetallic compounds on work in progress, extend our efforts to prepare and design molecules of interest for intramolecular electron and energy transfer, determine the photophysics of ligand loss from ruthenium(II) monometallic complexes and examine catalytic properties of our complexes. We have successfully made contributions toward each of these goals.

The preparation and properties of both homonuclear (same metal center) and heteronuclear (different metal centers) complexes containing from one to four metal centers were reported. The complexes exhibited a large number of redox active sites and some of them were weakly luminescent.

New complexes of rhenium(I) and platinum(II) which emitted strongly in solution and underwent excited state electron transfer were synthesized. A bimetallic complex containing rhenium(I) and ruthenium(II) exhibited unusual properties. Luminescence was observed from each metal core. Moreover, the data indicate that luminescence from the ruthenium(II) moiety is enhanced at the expense of luminescence from the rhenium(I) site. This enhancement was attributed to energy transfer.

The photophysics of tris-chelated ruthenium(II) and bis-chelated, bispyridine ruthenium(II) complexes was examined. Temperature dependent emission lifetimes were attributed to either energy loss through a fourth charge transfer excited state, the third MLCT state, or the dd state, depending upon the complex in question. The results of the study indicate that the "$Ru(bpz)(bpy)^{2+}$" core, where bpz is 2,2′-bipyrazine and bpy is 2,2′-bipyridine, would be least sensitive to photochemical ligand loss.

Catalytic properties were examined at surface modified electrodes. Significant photocurrents were observed in carrageenan, a polysaccharide hydrogel. Two hydrogel systems were examined. These were: (a) one containing $Ru(bpy)_3^{2+}$, methyl viologen and triethanolamine, and (b) one containing $Ru(bpy)_3^{2+}$, oxygen and triethanolamine.

Catalytic CO_2 reduction was also examined at a bare platinum electrode, at a bare platinum electrode in a solution containing $Co(bpy)_3^{3+}$ as a homogeneous catalyst, and at a platinum electrode whose surface was modified with a cobalt bipyridine-like material. Oxalate ion was the only reduction product found in these systems.

Personnel Involved in Research

Research Group:

A. Graduate Student and Research Associates

Chuck Blanton	Research Assistant	B.S.	Belmont Abbey
Massoud Boldaji	Research Assistant	B.S.	UNC-C
Ty Garber	Research Assistant	B.S.	Appalachian State
Hsin Hsi Lai	Research Assistant	B.S.	Fu-Jen Catholic Univ.
Philomena Matthews	Research Assistant	B.S.	University of Kerala
Helen Ross	Research Assistant	B.S.	UNC-C
Randy Shaver	Research Assistant	B.S.	Pfeiffer
Shirley Wang	Research Assistant	B.S.	Beijing Inst. of Chem. Tech.
Russell White	Research Assistant	M.S.	UNC-CH
June Yao	Research Assistant	B.S.	Beijing Normal Univ.
Sheuh-Lin Yau	Research Assistant	B.S.	Tunghai University
Don Jackman	Research Associate	Ph.D.	University of Tennessee
Shawn Van Wallendael	Research Associate	Ph.D.	Northwestern

B. Undergraduate Scholars

Larry Morgan

C. Graduate Degree Recipients

Sheuh-Lin Yau, 1987
Massoud Boldaji, 1988
Hsin Hsi Lai, 1988
Helen B. Ross, 1988
Philomena Matthews, 1989

List of Publications Resulting From DOE Research

38) "The Reactivity of [CuTIM]$^{2+}$ with Chloride Ion," D. E. Whitmoyer and D. P. Rillema, J. Chem. Soc., Chem. Commun. 1986, 677.

41) "A Ruthenium(II)/Platinum(II) Binuclear Complex Bridged by 2,2'- Bipyrimidine," R. Sahai and D. P. Rillema, Inorg. Chim. Acta. 1986, 118, L32.

42) "A Luminescing Ruthenium(II)/Platinum(II) Binuclear Complex," R. Sahai, D. A. Baucom and D. P. Rillema, Inorg. Chem. 1986, 25, 3843.

43) "Homonuclear and Heteronuclear Oligomers Containing Ruthenium(II) and Platinum(II)," R. Sahai and D. P. Rillema, J. Chem. Soc., Chem. Commun. 1986, 1133.

44) "Structure, Redox and Photophysical Properties of a Series of Ruthenium Heterocycles Based on the Ligand 2,3-Bis(2'-pyridyl)quinoxaline," D. P. Rillema, D. G. Tighdiri, D. S. Jones, C. D. Keller, L. A. Worl, T. J. Meyer, and H. A. Levy, Inorg. Chem. 1987, 26, 578.

46) "The Reactivity of [Cu(TIM)]$^{2+}$ with Pyridine: Formation Constants Determined by Cyclic Voltammetry," David E. Whitmoyer and D. Paul Rillema, Inorg. Chem. 1987, 26, 2012.

47) "Photophysical and Photochemical Properties of Ruthenium(II) Mixed-Ligand Complexes: Precursors to Homooligonuclear and Heterooligonuclear Complexes Containing Ruthenium(II), Platinum(II), Rhenium(I) and Rhodium(III)," D. Paul Rillema and Helen Ross, "The Seventh International Symposium on the Photochemistry and Photophysics of Coordination Compounds," Springer-Verlag, NY, 1987, 151.

49) "Ruthenium(II) Cluster Complexes: A Series of Homooligonuclear Complexes: Based on Bidentate Bridging Ligands," Ram Sahai, Larry Morgan and D. Paul Rillema, Inorg. Chem. 1988, 27, 3495.

51) "A Rapid Synthetic Method for the Preparation of Two Tris-Cobalt(III) Compounds," D. C. Jackman and D. P. Rillema, J. Chem. Educ. 1989, 66, 343.

54) "Complexes of Ruthenium(II) with $(bpm)Re(CO)_3Cl$ and $[HAT(Re(CO)_3Cl)_2]$ as Ligands: Syntheses, Redox and Luminescence Properties", Ram Sahai, D. Paul Rillema, R. J. Shaver, S. Van Wallendael, D. C. Jackman and M. Boldaji, Inorg Chem. 1989, 28, 1022.

55) "ESR Study of the Solution Thermochromism Resulting From Low-Temperature Isomerization of Some Pyrazolato-Bridged Dirhodium Complexes Generated via Electrochemical Oxidation," C. Woods, L. Totorelli, D. P. Rillema, J. L. E. Burn and J. DePriest, Inorg. Chem. 1989, 28, 1673.

56) "Photosubstitution in Tris-Chelate Complexes of Ruthenium(II) Containing the Ligands 2,2'-Bipyrazine, 2,2'-Bipyrimidine, 2,2'-Bipyridine and 4,4'-Dimethyl-2,2'-Bipyridine: Energy Gap Control," H. B. Ross, M. Boldaji, D. P. Rillema, C. B. Blanton, , and R. P. White, Inorg. Chem. 1989, 28, 1013.

57) "A Rhenium(I) Bipyrimidine Tricarbonyl Complex Containing Methyl Viologen as the Sixth Ligand: NMR and Structural Results," L. N. Winslow, D. Paul Rillema, Jane H. Welch and P. Singh, Inorg. Chem. 1989, 28, 1596.

59) "Ground State and Excited State Properties of Monometallic and Bimetallic Complexes Based on Rhenium Tricarbonyl Chloride: The Effect of an Insulating vs. a Conducting Bridge," S. Van Wallendael, R. J. Shaver, D. P. Rillema, B. J. Yoblinski, M. Stathis, and T. Guarr, submitted to Inorg. Chem..

60) "Multimetallic Ruthenium(II) Complexes Based on Biimidazole and Bibenzimidazole: The Effect of Dianionic Bridging Ligands on Redox and Spectral Properties," D. Paul Rillema, Ram Sahai, Philomena T. Matthews, A. K. Edwards, Randy J. Shaver and Larry Morgan, Inorg. Chem., in press.

61) "Highly Luminescing Rhenium(I) Heterocylic Ligand Tetracarbonyl Complexes," Randy J. Shaver, D. Paul Rillema and Clifton Woods, J. Chem. Soc., Chem. Commun., in press.

62) "Synthetic Control of MLCT Excited States. Control of the MLCT-dd Energy Gap in Bis-Pyridine Ruthenium(II) Heterocycles," Laura A. Worl, Thomas J. Meyer, Massoud Boldaji, Stephanie A. Bundy, D. Paul Rillema, and Charles B. Blanton, submitted to J. Phys. Chem..

63) "Carrageenan Hydrogel Immobilization of $Ru(bpy)_3^{2+}$ at an Electrode Surface. Electrochemistry and Photocurrents," S. C. Perine, A. K. Edwards, A. L. Crumbliss, and D. Paul Rillema, submitted to Inorg. Chem..

64) "Further ESR Studies of Pyrazolato-Bridged Thermochromic Dirhodium Complexes," James L. E. Burn, Clifton Woods an D. Paul Rillema, submitted to Inorg. Chem..

65) "Crystal and Molecular Structure of the Photocatalyst Tris(2,2'-Bipyrazine)ruthenium(II) Hexafluorophosphate," H. Li, D. S. Jones, D. C. Schwind and D. Paul Rillema, J. Cryst. Spectrosc. Res., in press.

66) "A Novel Copper(II) Complex Containing the Ligand 1,2-bis(2,2'-bipyridyl-6-yl)ethane: Structural, Magnetic, Redox and Spectral Properties," T. Garber, S. Van Wallendael, D. Paul Rillema, M. Kirk, W. E. Hatfield, J. H. Welch and P. Singh, submitted to Inorg. Chem.

67) "Efficient Preparative Routes to 6,6'-Dibromo-2,2'-bipyridine and 6-Bromo-2,2'-bipyridine," Ty Garber and D. Paul Rillema, submitted to Tetrahedron Letters.

68) "Synthetic Control of Excited-States: Electron Transfer From the 3π Level of the Biphenyl Dianion Coordinated to Platinum(II)," Charles B. Blanton and D. Paul Rillema, Inorg. Chim. Acta, in press.

In Preparation (Work in Progress Resulting from DOE Funded Research)

69) "Dual Luminescence from a Mixed-Metal Complex Containing Rhenium(I) and Ruthenium(II) Photochromophores," Shawn Van Wallendael and D. Paul Rillema, manuscript in preparation.
70) "Photocurrents Derived From $[Ru(bpy)_3]^{2+}$, Oxygen and Triethanolamine in a Hydrogel Matrix." A. Kirk Edwards and D. Paul Rillema, manuscript in preparation.
71) "Diffusion of Cations and Electron Hopping in a Hydrogel Matrix," S. C. Perine, A. Kirk Edwards, Alvin L. Crumbliss and D. Paul Rillema, manuscript in preparation.
72) "Redox, Structure and Photophysical Properties of $[(bpm)Re(CO)_3CH_3CN]PF_6$," Randy J. Shaver, Clifton Woods and D. Paul Rillema, manuscript in preparation.
73) "Photophysical Properties of 2-(2-Pyridyl)Pyrimidine Complexes of Ruthenium(II): Direct Population of Ligand Field States from the ^{1}MLCT State," Chuck B. Blanton, D. Paul Rillema, Randy J. Shaver and Linda N. Winslow, manuscript in preparation.
74) "Redox and Spectral Properties of a Series of Ruthenium(II)/Platinum(II) Heterooligonuclear Complexes: A New Series of Mixed-Metal Complexes," R. J. Shaver, Ram Sahai, Larry Morgan, and D. Paul Rillema, manuscript in preparation.
75) "Photophysical Properties of Platinum(II) Complexes Containing the Biphenyl Dianion as a Ligand: ^{3}MLCT vs. ^{3}CT Behavior," Chuck B. Blanton and D. Paul Rillema, manuscript in preparation.
76) "Preparation, Redox and Spectral Properties of a New Series of Ruthenium(II) Complexes Containing the Ligand 1,2-Bis(2,2'-bipyridyl-6-yl)Ethane," Xiao-Li Wang and D. Paul Rillema, manuscript in preparation.
77) "The Photophysical Properties of Rhenium(I) Tetracarbonyl Complexes," Randy J. Shaver and D. Paul Rillema, manuscript in preparation.
78) "The Structure of $[Co(acacen)py_2]PF_6$. A Case for Perpendicular Pyridine Rings," D. S. Jones, N. Nance, D. P. Rillema, and H. Levy, manuscript in preparation.
79) "The Reaction of $[Cu(TIM)]^{2+}$ with Chloride Ion: Stepwise Reactivity Involving A Chloro Bridged Species," Larry Morgan, D. C. Jackman, R. Ramette and D. Paul Rillema, manuscript in preparation.

List of Presentations Resulting from DOE Research

30) "Design and Properties of a Series of Ruthenium Photochromophores Based on the Ligand 2,3-Bis(2'-Pyridyl)Quinoxaline," D. Paul Rillema, The Ninth DOE Solar Photochemistry Conference, New Paltz, NY, June 2-6, 1985.
33) "Mixed Metal and Oligonuclear Compounds, Potential Multielectron Transfer Agents," D. Paul Rillema, The Tenth DOE Solar Photochemistry Conference, Niagra-on-the Lake, Canada, June 9-14, 1986.
34) "A Novel Mixed-Valent Homooligonuclear Metal Complex Containing One Inner Ruthenium(III) and Three Outer Ruthenium(II) Centers Bridged by 2,2'-Bibenzimidazole," R. Sahai and D. Paul Rillema, The Gordon Research Conference on Donor-Acceptor Complexes, Plymouth State College, Plymouth, NH, August 10-15, 1986.
35) "Homooligonuclear Complexes of Ruthenium(II) Heterocycles Containing Up to Four Metal Centers," Ram Sahai and D. Paul Rillema, The 192nd National ACS Meeting, Anaheim, CA, September 7-12, 1986.
36) "Heterooligonuclear Complexes of Ruthenium(II) Heterocycles Containing Up to Three Platinum(II) Metal Centers," Ram Sahai and D. Paul Rillema, The 192nd National ACS Meeting, September 7-12, 1986.
39) "Photophysical and Photochemical Properties of Ruthenium(II) Mixed-Ligand Complexes: Precursors to Homooligonuclear and Heterooligonuclear Complexes Containing Ruthenium(II), Platinum(II), Rhenium(I) and Rhodium(III)", D. Paul Rillema and Helen B. Ross, The Seventh International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Elmau, Germany, March 30 - April 2, 1987.

40) "Photosubstitution in Ruthenium(II) Heterocycles: Displacement of the Ligand with the Lowest Energy π^* Level," H. B. Ross, D. Paul Rillema and Russell P. White, The Eleventh DOE Solar Photochemistry Conference, Lake Tahoe, CA, June 7-11, 1987.

42) "Homooligonuclear Complexes of Ruthenium(II): The Effect of π^* Donor Bridging Ligands on Redox and Spectral Properties," D. Paul Rillema, R. Sahai, L. Morgan and P. Matthews, The 194th National ACS Meeting, New Orleans, LA. August 30-September 4, 1987.

43) "Photophysical Properties of Multimetallic Complexes and Their Precursors," D. Paul Rillema, The Twelfth Solar Photochemistry Research Conference, Airlie, VA, May 22-26, 1988.

44) "Photophysical Properties of Bis-Pyridine Ruthenium(II) Heterocycles," D. Paul Rillema, Massoud Boldaji, Laura Worl and T. J. Meyer, The 3rd Chemical Congress of North America, Toronto, Canada, June 5-10, 1988.

45) "Luminescence Properties of Multimetallic Complexes Containing Ruthenium(II), Rhenium(I), and Platinum(II)," D. Paul Rillema, Shawn Van Wallendael, Randy Shaver, Ram Sahai and Philomena Matthews, XII IUPAC Symposium on Photochemistry, Bologna, Italy, July 17-23, 1988.

46) "Ground State and Excited State Properties of Monometallic and Bimetallic Complexes Based on Rhenium(I) Tricarbonyl Chloride: The Effect of an Insulating vs. a Conducting Bridging Ligand," D. Paul Rillema, Shawn Van Wallendael and Randy J. Shaver, The 197th National ACS Meeting, Dallas, Texas, April 9-14, 1989.

47) Hydrogel Immobilization of Tris(2,2'-Bipyridyl)Ruthenium(II) and Methyl Viologen at an Electrode Surface: Electrochemistry and Photocurrents," Sherry C. Perine, A. L. Crumbliss, A. Kirk Edwards and D. Paul Rillema, The 197th National ACS Meeting, Dallas, Texas, April 9-14, 1989.

48) "Design and Properties of Rhenium(I) Carbonyl Complexes Containing Heterocyclic Bridging Ligands: Bimetallic and Donor-Acceptor Complexes," The Thirteenth Solar Photochemistry Research Conference, Silver Creek, CO, June 12-15, 1989.

49) "Highly Luminescing Rhenium(I) Tetracarbonyl Complexes Containing Bidentate Heterocyclic Ligands," Randy J. Shaver and D. Paul Rillema, The Eighth International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Santa Barbara, CA, August 13-18, 1989.

52) "Synthesis, Redox and Spectral Properties of Bipyrimidine and 2,3-Bis(2-pyridyl)quinoxaline Bridged Ruthenium(II)/Platinum(II) Complexes," R. P. White, R. Sahai and D. Paul Rillema, The 41st American Chemical Society Southeast Regional Meeting, Winston Salem, NC, Oct. 9-11, 1989.

53) "A Novel Copper(II) Complex Containing the Ligands 1,2-Bis(2,2'-bipyridyl- 6-yl)Ethane. Structural, Magnetic, Redox and Spectral Properties," T. H. Garber, S. Van Wallendael, D. Paul Rillema, M. Kirk, W. E. Hatfield, J. H. Welch and P. Singh, The 41st American Chemical Society Southeast Regional Meeting, Winston-Salem, NC, Oct. 9-11, 1989.

54) "Studies of Pyrazolato-Bridged Binuclear and Tetranuclear Rhodium Complexes," L. J. Tortorelli, J. E. Burns, C. Woods and D. Paul Rillema, The 41st American Chemical Society Southeast Regional Meeting, Winston-Salem, NC, Oct. 9-11, 1989.

55) A Photoelectrode Based on Immobilization of Tris(2,2'-bipyridyl)ruthenium(II) and Methylviologen in a Hydrogel on a Platinum Surface," A. K. Edwards, D. Paul Rillema, A. L. Crumbliss and S. C. Perine, The 41st American Chemical Society Southeast Regional Meeting, Winston-Salem, NC, Oct. 9-11, 1989.

56) "Synthesis and Characterization of a Series of Ruthenium Complexes Containing the Ligand 2-(2-pyridyl)pyrimidine," C. B. Blanton, D. Paul Rillema and L. N. Winslow, The 41st American Chemical Society Southeast Regional Meeting, Winston-Salem, NC, Oct. 9-11, 1989.

57) "Highly Luminescing Rhenium(I) Tetracarbonyl Complexes Containing Bidentate Heterocyclic Ligands," R. J. Shaver, S. Van Wallendael, D. Paul Rillema and C. Woods, The 41st American Chemical Society Southeast Regional Meeting, Winston-Salem, NC, Oct. 9-11, 1989.

58) "Dual Emission From a Mixed-Metal Ruthenium(II)/Rhenium(I) Complex: Isolated Photochromophores," S. Van Wallendael and D. Paul Rillema, The 41st American Chemical Society Southeast Regional Meeting, Winston-Salem, NC, Oct. 9-11, 1989.

59) "Synthesis of Open Ended Macrocycles Based on 2,2'-Bipyridine," T. H. Garber, S. Van Wallendael and D. Paul Rillema, The 41st American Chemical Society Southeast Regional Meeting, Winston-Salem, NC, Oct. 9-11, 1989.

Additional Support.

The National Science Foundation funded ($33,933) a project entitled, "Acquisition of a High Speed Transient Digitizer and a Low Temperature Dewar for Elucidating the Excited State Properties of Novel Oligonuclear and Mixed-Metal Complexes." The equipment purchased with this grant include an IBM Model 60 computer, a LeCroy transient digitizer containing 1.3 Gigasample/s and 200 MHz plug-in units and a Cryo low temperature dewar.

The Foundation of The University of North Carolina at Charlotte has provided funding to support the research activity of two graduate students ($4100 summer of 1989) and $4100 towards the purchase of a boxcar integrator (summer of 1988).

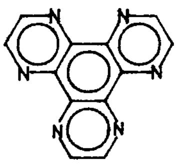
In addition, the Office of Energy Science of the Department of Energy provided supplemental support of $51,781 to acquire a research grade luminescence spectrophotometer (Spex 212).

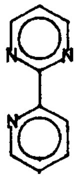
NARRATIVE

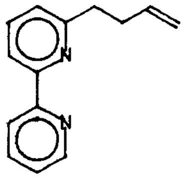
Progress of Project During the Time Period 1/1/87 - 1/1/90

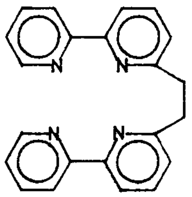
Preparations.

1. Ligands. Additional ligands for effecting attachment of metals, either singly or in clusters, have been synthesized. The ligand HAT, py-pm, O-BPY and 6-R-bpy shown below were prepared in the course of our investigations. The HAT ligand was prepared by a modification of Rogers procedure. [Rogers, D. Z. J. Org. Chem. 1986, 51, 3904]. The py-pm ligand was prepared according to the procedure of Lafferty and Case. [Lafferty, J. J.; Case, F. H. J. Org. Chem. 1967, 32, 1591].


HAT


py−pm


6−R−bpy

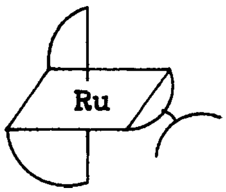

o−BPY

The O-BPY and 6-R-bpy ligands were synthesized by new procedures under exploration in our laboratories. The methods involve metallation, metal-halogen exchange and cuprate coupling reactions with organic molecules. Examples of our successes to date follow. The basic molecule 6-methyl-2,2′-bipyridine was used to prepare O-BPY and 6-R-bpy. It was synthesized by the reaction of methyllithium with 2,2′-bipyridine. O-BPY was then prepared by addition of lithium diisopropylamide to a cold solution of 6-methyl-2,2′-bipyridine and two metallated fragments were then coupled by addition of dibromoethane. Addition of 1,3-dibromopropane rather than dibromoethane resulted in formation of 6-R-bpy. The mechanism accounting for coupling is electron exchange, the mechanism accounting for addition of the alkyl chain is double halogen elimination. Other precursors which we have recently prepared for designing macrocyclic ligands based on 2,2′-bipyridine are 6,6′-dibromo-2,2′-bipyridine and 6-bromo-2,2′-bipyridine.

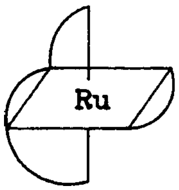
2. Monometallic Complexes.

a. Ruthenium(II). The series $[Ru(bpy)_2HAT](PF_6)_2$, $[(Ru(bpy)_2)_2HAT](PF_6)_4$ and $[(Ru(bpy)_2)_3HAT](PF_6)_6$ and $[Ru(bpy)_2(py\text{-}pm)](PF_6)_2$, $[Ru(bpy)(py\text{-}pm)_2](PF_6)_2$, and

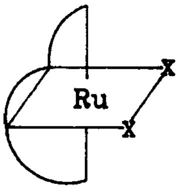
[Ru(py-pm)$_3$](PF$_6$)$_2$ were prepared. The synthesis of the ruthenium(II) series illustrated below is



[Ru(bpy)$_2$(o-BPY)]$^{2+}$

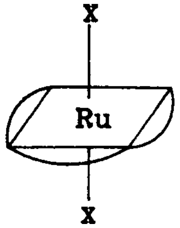


[Ru(bpy)(o-BPY)]$^{2+}$



cis-[Ru(o-BPY)X$_2$]

and
or



trans-[Ru(o-BPY)X$_2$]

underway. Complexes containing all three of the formulations above have been prepared based on vis/uv, redox and elemental analysis data. The stereochemistry of Ru(O-BPY)Cl$_2$ remains undetermined. Crystals are currently being grown to answer that question by way of an X-ray structure analysis.

b. <u>Rhenium(I)</u>. Three different types of rhenium(I) complexes were investigated. These were tetracarbonyl derivatives, a tricarbonyl acetonitrile complex, and tricarbonyl pyridine derivatives.

The rhenium(I) tetracrabonyl heterocyclic ligand complexes [Re(CO)$_4$(L-L)]PF$_6$, where L-L is 2,2′-bipyridmidine (bpm), 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmb) and 1,10-phenanthroline (phen) were prepared. These represent a <u>new</u> class of previously unreported compounds with high emission energies, fairly long excited-state lifetimes and excited states that behave as powerful oxidants. A crystal structure of [(bpm)Re(CO)$_4$]BF$_4$ revealed that the Re-C(CO) bond distance for CO ligands trans to each other was 2.03 Å but 1.93 Å for CO ligands trans to bpm.

The rhenium(I) tricarbonyl acetonitrile complex was isolated as the PF$_6^-$ salt. An X-ray structure of [(bpm)Re(CO)$_3$(CH$_3$CN)]PF$_6$ indicated that the Re-C(CO) bond distance was 1.91 Å for CO ligands trans to bpm and 1.94 Å for the CO ligand trans to CH$_3$CN. The Re-N bond distance to the nitrogen atoms of the bpm ligand was 2.18 Å but it was 2.09 Å to the nitrogen atom of acetonitrile.

A number of rhenium(I) tricarbonyl "pyridine" complexes were synthesized. These were [(bpm)Re(CO)$_3$py](PF$_6$), [(dmb)Re(CO)$_3$py](PF$_6$), [(Mebpy-Mebpy)Re(CO)$_3$py](PF$_6$) and [(bpm)Re(CO)$_3$MeQ](PF$_6$)$_2$, where Mebpy-Mebpy is 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane and MeQ$^+$ is N-methyl-4,4′-bipyridinium ion. A crystal structure of [(bpm)Re(CO)$_3$MeQ](PF$_6$)$_2$ revealed that the geometry of the cation is facial. It also indicated that there was a 9° twist of the pyrimidine rings from planarity, a 38° twist between the py and Mepy component of the MeQ ligand, a Re-N(bpm) bond distance of 2.17 Å and Re-N(MeQ) bond distance of 2.21 Å.

c. Platinum. Platinum(II) complexes with room temperature luminescing properties in solution were isolated. The complexes were derived from $[Pt(bph)(C_2H_5)_2S]_2$, where bph is the dianion of biphenyl and $(C_2H_5)_2S$ is diethyl sulfide. The derivatives include [(en)Pt(bph)], $[(CH_3CN)_2Pt(bph)]$ and $[(py)_2Pt(bph)]$, where py is pyridine and en is ethylenediamine, and display fairly intense ^3CT luminescence in methylene chloride or acetonitrile. Dissolution of $[(CH_3CN)_2Pt(bph)]$ in methylene chloride results in slow precipitation of a material that luminesces strongly in the solid state and is insoluble in all solvents tested. The material most likely consists of bridging Pt-CH_3CN-Pt units.

d. Cobalt. The possibility of preparing mixed ligand complexes of cobalt(III) was investigated. $[Co(bpy)_2Cl_2]Cl \cdot 2H_2O$ was prepared by literature methods [Hancock, M. P.; Josephson, J.; Schaffer, C. E. Acta Chemica Scandinavica 1976, 30, 79]. Reaction of $[Co(bpy)_2Cl_2]Cl$ with other bidentate heterocyclic ligands such as bpm and bpz to form mixed ligand complexes met with limited success. $[Co(bpy)_3]^{3+}$ was found to be a product along with other statistical possibilities such as $[Co(bpy)_2(bpm)]^{3+}$, $[Co(bpm)_2(bpy)]^{3+}$, etc.

$Na_3[Co(C_2O_4)_3]$ was found to be a versatile starting material for the preparation of tris chelates. $[Co(bpy)_3](PF_6)_3$ and $[Co(bpm)_3](PF_6)_3$ were readily prepared by the reaction of $Na_3[Co(C_2O_4)_3]$ with an excess of the appropriate heterocyclic ligand in the presence of activated charcoal. The preparation proceeds more rapidly than the Cl_2 oxidation procedure which we reported earlier.

Anhydrous $CoCl_2$ proved to be a useful starting material for the preparation of $[Co(bpy)_3](PF_6)_2$. However, reaction of $CoCl_2$ with excess Mebpy-Mebpy resulted in the formation of a nonstoichiometric compound of composition $[Co_{1.2}(Mebpy\text{-}Mebpy)_2](PF_6)_{2.4.}$ The compound adsorbs on electrode surfaces upon reductive cycling and enhances the current associated with reduction of CO_2 to oxalate ion.

e. Copper. $[Cu(O\text{-}BPY)](ClO_4)_2$ was prepared and reduced to $[Cu(O\text{-}BPY)](ClO_4)$ with ascorbic acid. A crystal structure of $[Cu(O\text{-}BPY)](ClO_4)_2$ revealed that the O-BPY ligand was distorted from planarity as expected due to the presence of the ethyl bridge. Co-N bond distances were 2.02 Å for the nitrogen atoms adjacent to the bridge and 1.99 Å for the nitrogen atoms remote from the bridge.

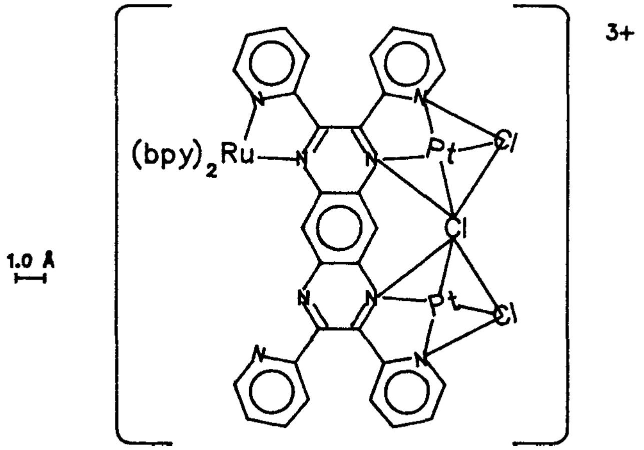
3. Multimetallic Complexes.

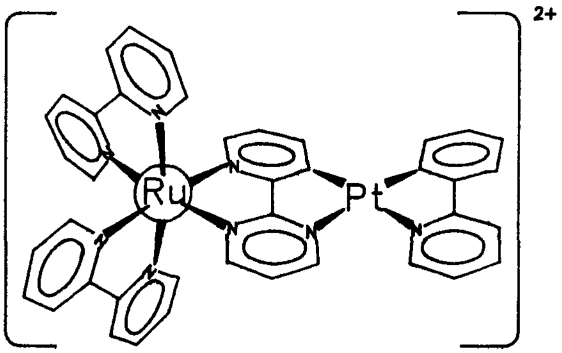
a. Ruthenium(II)/Rhenium(I) Complexes. The synthesis of the series $[(bpy)_nRu(bpmRe(CO)_3Cl)_{3-n}]^{2+}$, where n varied from zero to two, was completed. $[(bpy)_2RuHAT(Re(CO)_3Cl)_2]^{2+}$ was also prepared and its properties were compared to the bpm series. The preparations were affected by the reaction of the appropriate precursor complex, $[Ru(bpy)_2bpm]^{2+}$, $[Ru(bpy)(bpm)_2]^{2+}$, $[Ru(bpm)_3]^{2+}$ or $[Ru(bpy)_2HAT]^{2+}$ with $Re(CO)_5Cl$ in methanol.

A series of Ru(II)/Re(I) complexes based on $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3L]^{3+}$, where L = py, MeQ^+ and Py-PTZ, were also synthesized. The $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$ complex exhibits dual luminescence - a property that may lead to a better understanding of charge separation in multimetallic complexes.

b. Ruthenium(II)/Cobalt(III) Complexes. The molecule $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Co(bpy)_2]^{5+}$ was prepared by the reaction of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ with $[Co(bpy)_2Cl_2]^+$. Photophysical studies are underway in collaboration with John Endicott's research group. Preliminary studies reveal that the excited state lifetime of the bimetallic complex is an order of magnitude lower than for $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+*}$. Further, the rate of quenching indicated an intramolecular process predominated rather than intermolecular electron transfer.

c. Ruthenium(II)/Platinum(II) Complexes. Two different types of ruthenium(II)/platinum(II) bimetallic complexes shown below were proposed for study. These were orthometallated and





chlorobridged species. The precursor for forming the orthometallated bimetallic complex, $[Ru(bpy)_2(py\text{-}pm)]^{2+}$, was prepared. The basic idea was to metallate the carbon atom α to the bridge (metallation here means substitution of C-H bound hydrogen with lithium) and then effect complex formation between the metallated carbon atom and the remote nitrogen atom of (py-pm). Metallation studies of both py-pm and $[(bpy)_2Ru(py\text{-}pm)]^{2+}$ were carried out but metallation was not stereospecific. Hence preparations of orthometallated bimetallic complexes was abandoned in favor of using the $[(bph)Pt(C_2H_5)_2S]_2$ precursor.

The preparation and properties of the chlorobridged species has also been investigated. A complex whose elemental analysis is consistent with the proposed structure in the figure above has been isolated. The complex is paramagnetic and gives an anisotropic epr spectrum with g-values of 2.06, 2.02 and 1.98. The esr spectrum is consistent with the unpaired electron localized on a metal center suggesting, perhaps, that one platinum is present in the +2 oxidation state and the other is in the +1 oxidation state.

Properties.

1. Synthetic Control of MLCT States in Ruthenium(II) Complexes. A number of our studies have focused on the problem of photosubstitution in ruthenium(II) polypyridyl complexes. Our goal was to minimize its occurrence by synthetic control. Photosubstitution quantum yields of the complexes $[Ru(bpz)_2bpm]^{2+}$, $[Ru(bpm)_2bpz]^{2+}$, $[Ru(bpz)(bpm)(bpy)]^{2+}$, $[Ru(bpm)_2(CH_3CN)Cl]^+$, $[Ru(bpz)_2(CH_3CN)Cl]^+$, and $[Ru(L\text{-}L)_2py_2]^{2+}$(L-L = dmb, bpy, bpm, bpz) and $[Ru(bpy)_n(L'\text{-}L')_{3-n}]^{2+}$ (n = 0-3, L′-L′ = bpz, bpm) were studied in acetonitrile containing 1 mM Cl^- at room temperature (25 ± 0.1 °C). The substitution quantum yields ranged from 0.35 for $[Ru(bpz)_3]^{2+}$ to 1.7×10^{-4} for $[Ru(bpy)_2(bpz)]^{2+}$. The logarithm of the observed photochemical substitution quantum yield was found to correlate linearly with $\Delta E_{1/2}$, where $\Delta E_{1/2}$ is the difference in redox potential between the first oxidation and first reduction of the rutheniun complexes. Under a set of limiting conditions, the correlation of ϕ_p(obs) with $\Delta E_{1/2}$ was shown to relate to the energy gap law.

Temperature dependent excited state lifetime measurements of the bispyridine complexes provided additional information of value. Both radiative (k_r) and nonradiative (k_{nr}) rate constants and kinetics parameters suggested the intervention of an additional excited state in order to account for the photophysical parameters. The results also indicate that future complexes based on the "$Ru(bpy)(bpz)^{2+}$" core would be less likely to undergo photochemical degredation.

2. **Dual Luminescence in $[(bpy)_2Ru(Mebpy\text{-}Mebpy)Re(CO)_3py]^{3+}$.** The complex emits at 538 and at 610 nm when excited at 355 nm in methylene chloride at room temperature. The emission at 538 nm was found to be rhenium based; the one centered at 610 nm was assigned to the ruthenium(II) component. When photophysical properties of the bimetallic complex are compared to those of the monometallic precursors, $[Mebpy\text{-}MebpyRe(CO)_3py]^+$ and $[Mebpy\text{-}MebpyRu(bpy)_2]^{2+}$, the emission quantum yield was found to decrease from 0.11 to 0.009 on the rhenium(I) end but increase from 0.03 to 0.06 on the ruthenium side. The enhancement of the ruthenium-based emission at the expense of the rhenium-based emission has been attribued to energy transfer.

Transient absorption spectra of the three species cited above were obtained at UNC-Chapel Hill. As shown in Figure 1 on the next page, a large positive peak at ~370 nm is obtained for all three complexes and a negative peak related to bleaching of the MLCT (metal to ligand charge transfer) absorption band of the "$Ru(bpy)_3^{2+}$" component occurs when it is present. The 370 nm peak has been attributed to "bpy^{-1}", formed by photoelectron transfer from the metal to "bpy". The bleach is shallower in the bimetallic complex which is in agreement with populating excited states on both the rhenium side and the ruthenium side of the bimetallic complex. In addition, absorption decay rates were similar to luminescence decay rates. These observations indicate that the species giving rise to the transient absorbance is most likely the same transient that gives rise to luminescence.

3. **Highly Luminescing Compounds of Rhenium(I) and Platinum(II).** Table 1 contains data related to the luminescence properties of $[(L\text{-}L)Re(CO)_3py]^+$, where L-L = dmb and Mebpy-Mebpy, $[(L'\text{-}L')Re(CO)_4]^+$, where L′-L′ = bpm, bpy and phen, and $[(bph)PtL_2]$, where $L_2 = py_2$, ethylenediamine or $(CH_3CN)_2$. The radiative quantum yields are on the order of 0.1 except for $[(bpm)Re(CO)_4]^+$ (ϕ_r = 0.05), $[(bph)Pt(CH_3CN)_2]$ ($\phi_r = 0.03$) and $[(bph)Pt(py)_2]$ ($\phi_r = 0.04$). The excited state lifetimes are on the order of microseconds with a low value of 0.39 μs for $[(bpm)Re(CO)_4]^{+*}$ to a high value of 14 μs for

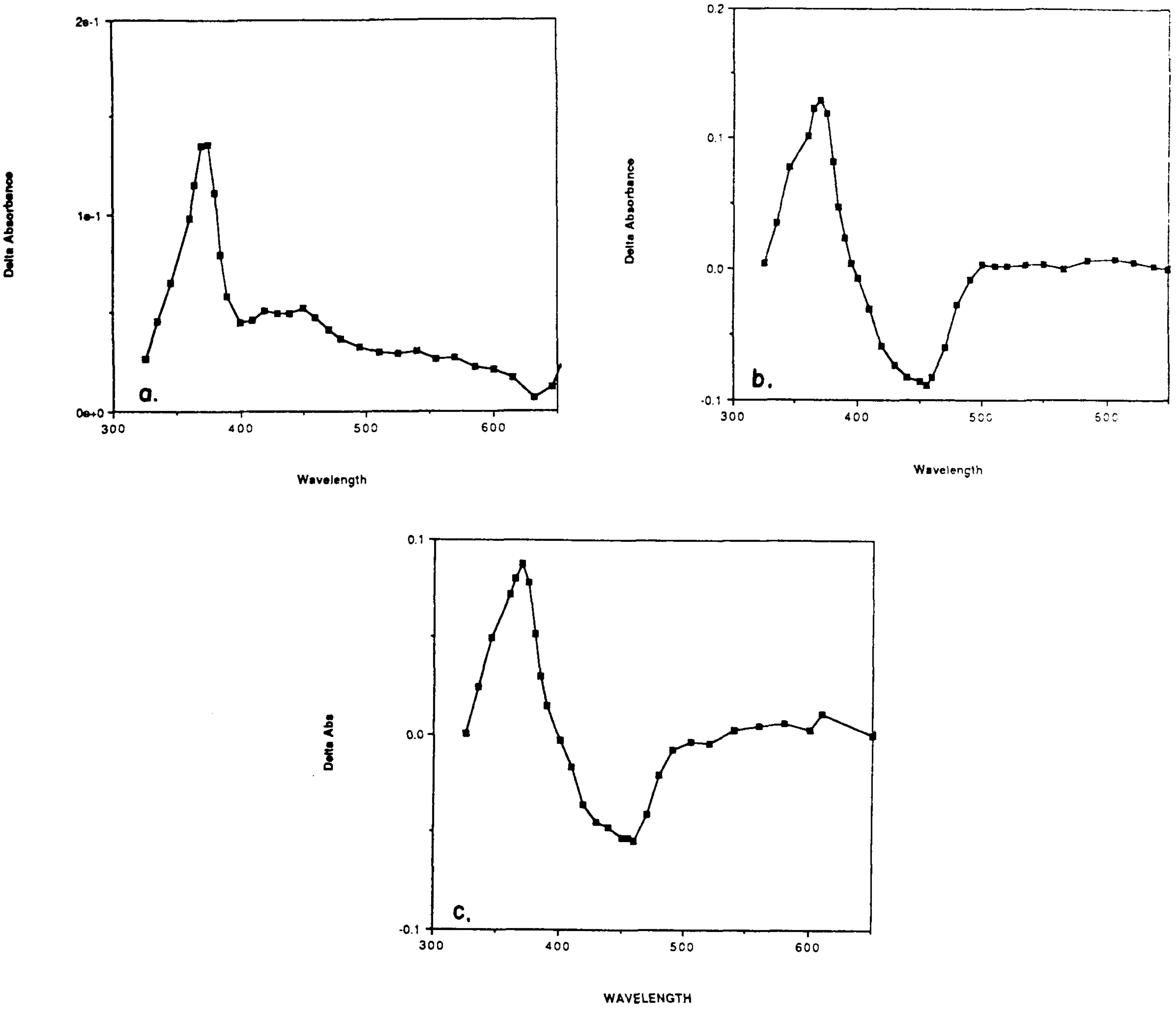


Figure 1. Transient absorption spectra 30 ns after the flash for
a. [Mebpy–MebpyRe(CO)$_3$py]$^{+}$,
b. [(bpy)$_2$Ru(Mebpy–Mebpy)]$^{2+}$,
c. [(bpy)$_2$RuMebpy–MebpyRe(CO)$_3$py]$^{3+}$.

Table I.

Luminescence Properties of Recently Synthesized Rhenium(I) and Platinum(II) Complexes.[a]

Compounds	$\lambda_{obs}(d\pi \dashrightarrow \pi^*)^c$	λ_{ex}, nm[c]	λ_{em}, nm[c]	τ_o,[d]ns	$\phi_r(25^o)^d$
$[(dmb)Re(CO)_3py]^+$	351 (4.7x10^3)	355	548	893	0.10
$[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$	354 (4.7x 0^3)	355	550	945	0.11
$[(bpm)Re(CO)_4]^+$	319 (3.2x10^3)	355	543	390	0.050
$[(bpy)Re(CO)_4]^+$	315 (1.5x10^4) 305 (1.4x10^4)	355	512	1040	0.099
$[(phen)Re(CO)_4]^+$	357 (2.1x10^3) 340 (2.4x10^3)	355	532	4050	0.11
$[(bph)Pt(CH_3CN)_2]^b$	325 (1.6x10^4)	355	493	14000	0.032
$[(bph)Pt(en)]^b$	333 (6.02 x 10^3)	355	493	4450	0.15
$[(bph)Pt(py)_2]$	331 (3.95x10^3)	355	493	3160	0.036

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a. Room temperature in degassed methylene chloride, except as indicated

b. acetonitrile

c. ± 1 nm, e ± 0.1 x 10^n

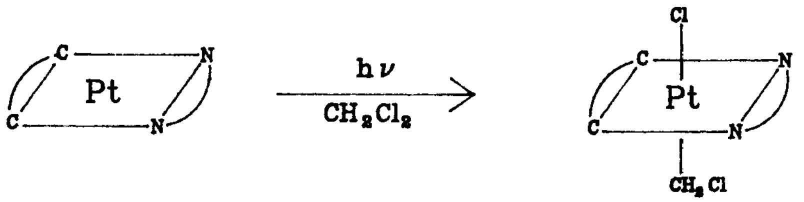
d. ± 10%

$[(bph)Pt(CH_3CN)_2]^*$. These high quantum yields and long lifetimes offer potential for their use in multimetallic complexes where radiative processes are partially quenched due to the heavy atom effect.

4. **<u>^{3}CT vs. ^{3}MLCT States</u>.** Emission from $[(bph)PtL_2]$, where $L_2 = py_2$, $(CH_3CN)_2$ and ethylenediamine, can be assigned to the ^{3}CT state. This emission contains well defined vibrational progressions of 1260 cm^{-1} corresponding to ring stretching modes of the bph ligand. Superimposed on the large progressions are additional vibrational modes separated by approximately 400 cm^{-1} which most likely are due to metal-ligand vibrations.

Emission from $[(bph)PtL_2]$, where L_2 = bpy, dmb, and phen, differ markedly from the above behavior. The emission is less intense and the emission manifold lacks vibrational components. In these systems, the π^* energy levels of the heterocyclic ligands are lower in energy than the π^* levels in bph, hence the excited state is assigned as the ^{3}MLCT state.

The photochemistry from the two states also differs. The quantum yield for oxidative addition given in eq. 1 was examined. The quantum yield for addition of CH_2Cl_2 to [(bph)Pt(dmb)] was 0.14 when excited at 355 nm but 0.031 when excited at 436 nm. Photoxidation was clearly favored for the higher energy excitation (population of the ^{3}CT state).



[(bph)Pt(dmb)] **[(bph)Pt(dmb)Cl(CH$_2$Cl)]** (1)

5. **<u>Reductive vs. Oxidative Quenching</u>.** Examination of the redox properties of $[Pt(bph)(CH_3CN)_2]$ and $[(bpm)Re(CO)_4]^+$ over the voltage range from +2.0 to -2.0 V vs. SSCE revealed interesting differences. For $[Pt(bph)(CH_3CN)_2]$, an irreversible oxidation was found at 0.85 V, but no reductions were observed. $[(bpm)Re(CO)_4]^+$, on the other hand, displayed a reduction at -0.87 V, but no oxidations were found. Calculation of potentials for their excited state redox couples, which were estimated by the difference in emission energy in eV and the potential of the ground state redox couple, indicated that $[Pt(bpy)(CH_3CN)_2]^*$ would be a powerful reductant whereas $[(bpm)Re(CO)_4]^{+*}$ would be a powerful oxidant.

Experimentally, oxidative quenching was varified for $[Pt(bph)(CH_3CN)_2]^*$ by reaction with methyl viologen (MV^{2+}) in acetonitrile as illustrated in eq. 2. Stern-Volmer behavior was

$$[Pt(bph)(CH_3CN)_2]^* + MV^{2+} \xrightarrow{kq} [Pt(bph)(CH_3CN)_2]^+ + MV^+ \qquad (2)$$

followed with $K_{SV} = 1.3 \times 10^5\ M^{-1}$. Based on this, kq was calculated to be $9.6 \times 10^9\ M^{-1}s^{-1}$.

Reductive quenching was varified for $[(bpm)Re(CO)_4]^{+*}$ by reaction with trimethoxybenzene (TMB) and chloride ion. The Stern-Volmer constant for the reaction in eq. 3 was 1277 M^{-1}

$$[(bpm)Re(CO)_4]^+ + TMB \xrightarrow{kq} [(bpm)Re(CO)_4] + TMB^+ \qquad (3)$$

and the quenching rate constant was $3.2 \times 10^9\ M^{-1}s^{-1}$. Similarly, quenching by Cl^- as measured by both luminescence and lifetime changes followed Stern-Volmer behavior indicating that the Cl^- quenching process was dynamic as opposed to static.

6. The Diagonal Correlation in Multielectron Redox Processes in Ruthenium/Platinum Complexes. Table II contains cyclic voltammetry data for the series $[(bpy)_nRu(bpmPtCl_2)_{3-n}]^{2+}$, where n = 0, 1, 2. The data lists reductions of the coordinated bpm ligands which occur at more positive potential than reductions associated with coordinated bpy ligands. Based on earlier work, each heterocyclic ligand can be reduced twice but the spacing between the first and second reduction is typically on the order of one volt. Thus, the first reduction of $[(bpm)_2Ru(bpmPtCl_2)]^{2+}$ occurs at -0.34 V and the second reduction occurs at -1.01 V. These successive processes are illustrated in eqs. 4 & 5. In addition, each coordinated bpm ligand is reduced first prior to a second reduction. Thus, -0.17 V, -0.30 V

$$[(bpy)_2Ru(bpmPtCl_2)]^{2+} + e^- \longrightarrow [(bpy)_2Ru(bpm^{-1}PtCl_2)]^+ \qquad (4)$$

$$[(bpy)_2Ru(bpm^{-1}PtCl_2)]^+ + e^- \longrightarrow [(bpy)_2Ru(bpm^{-2}PtCl_2)]^o \qquad (5)$$

Table II.

Electrochemical Data for Heterooligonuclear and Related bpm Complexes of Ruthenium(II) and Platinum(II)[a]

Compound	Reduction					
	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	$E_{1/2}(4)$	$E_{1/2}(5)$	$E_{1/2}(6)$
$[Pt(bpm)Cl_2]$	-0.88					
$[Ru(bpy)_2(bpm)]^{2+}$	-1.01					
$[(bpy)_2Ru(bpmPtcl_2)]^{2+}$	-0.34	-1.01				
$[(bpy)Ru(bpmPtCl_2)_2]^{2+}$	-0.25	-0.40	-1.03	-1.16		
$[Ru(bpmPtCl_2)_3]^{2+}$	-0.17	-0.30	-0.43	-1.00	-1.13	-1.32

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[a] Sweep Rate: 200 mv/s
Propylene Carbonate or Acetonitrile
Electrolyte: 0.10 M TEAP
Pt Working Electrode
vs. SSCE
Potentials ± 0.002V

and -0.43 V correspond to the reduction of successive bpm ligands in $[Ru(bpmPtCl_2)_3]^{2+}$ prior to a second series of reductions located at -1.00 V, -1.13 V and -1.32 V.

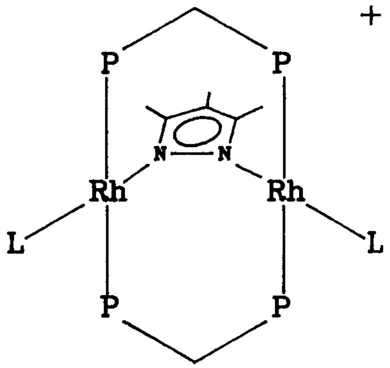
The first reduction of the bimetallic complex (-0.34 V) is shifted to more positive potential (-1.10 V) compared to the monometallic species. This shift has been attributed to electrostatic lowering of the π^* energy levels of the heterocyclic bridging ligand by the incoming positive charge of the metal ion. It is interesting to note the effect of successive reductions on the redox behavior with respect to this π^* energy level lowering. $E_{1/2}(2)$ of the bimetallic complex is similar to $E_{1/2}(1)$ of the monometallic complex; $E_{1/2}(3)$ of the trimetallic complex is similar to $E_{1/2}(2)$ of the bimetallic complex and $E_{1/2}(4)$ of the tetrametallic complex is similar to $E_{1/2}(3)$ of the trimetallic species. This sequence gives rise to the diagonal relationships illustrated in Table II. The added electrons apparently offset the positive charge of the added metal centers in a systemmatic way.

7. <u>Electrostatic Effects of Coordinated Ligands</u>. A series of Ruthenium(II) oligomers based on the bridging ligands biimidazole and bibenzimidazole give a rather clear understanding of the role electrostatic charges play in effecting ground state and excited state redox properties. Deprotonation of $[Ru(bpy)_2BiBzImH_2]^{2+}$ to give $[Ru(bpy)_2(BiBzIm)]^{\circ}$ shifted the potential from 0.91 V to -0.21 V. This effect was present in the series $[(bpy)_2Ru(BiBzImRu(bpy)_2)]^{2+}$, $[(bpy)Ru(BiBzImRu(bpy)_2)_2]^{2+}$ and $[Ru(BiBzImRu(bpy)_2)_3]^{2+}$ but to a lesser extent due to addition of positive charge from "$Ru(bpy)_2^{2+}$" units. The $Ru^{3+/2+}$ potentials for the oligomer series are 0.76 V, 0.32 V, and -0.26 V, respectively. Since excited state potentials can be related to the difference in potential of emission maximum in eV and the ground state redox potentials, the electrostatic charge of the ligand represents another way to control excited state properties.

8. <u>The Effect of an Insulating vs. a Conducting Bridge</u>. The effect that a coordinated metal ion has on remote ligand sites was examined by NMR spectroscopy. The ligand systems chosen to examine were bpm, bpp, and Mebpy-Mebpy, where bpp is 2,3-bis(2-pyridyl)pyrazine. The metal complex chosen was "$Re(CO)_3Cl$" due to the fact that it binds only one bidentate ligand at a time. Thus, the systems examined were $[(bpm)Re(CO)_3Cl]$, $[(bpp)Re(CO)_3Cl]$, $[(Mebpy\text{-}Mebpy)Re(CO)_3Cl]$, $[(bpm)(Re(CO)_3Cl)_2]$, $[(bpp)(Re(CO)_3Cl)_2]$, $[(Mebpy\text{-}Mebpy)(Re(CO)_3Cl)_2]$ and the free ligands.

The details of the study were presented in a paper recently submitted to Inorg. Chem. entitled "Ground State and Excited State Properties of Monometallic and Bimetallic Complexes Based on Rhenium(I) Tricarbonyl Chloride: The Effect of an Insulating vs. a Conducting Bridge." In summary, NMR properties revealed that protons on carbon atoms α to the coordinating nitrogen atoms of the coordinated heterocycles were deshielded and the resonance shifted downfield. For conducting bridges such as bpm, proton resonances of protons located on carbon atom α to uncoordinated nitrogen atoms also shifted downfield, but to a lesser extent. In contrast, little change in resonance position was noted for the uncoordinated protons of the Mebpy-Mebpy ligand indicating that the ethyl bridge segregates one side of the ligand from the other. The behavior of the bpp ligand was in between that of bpm and Mebpy-Mebpy as expected due to its intermediary nature.

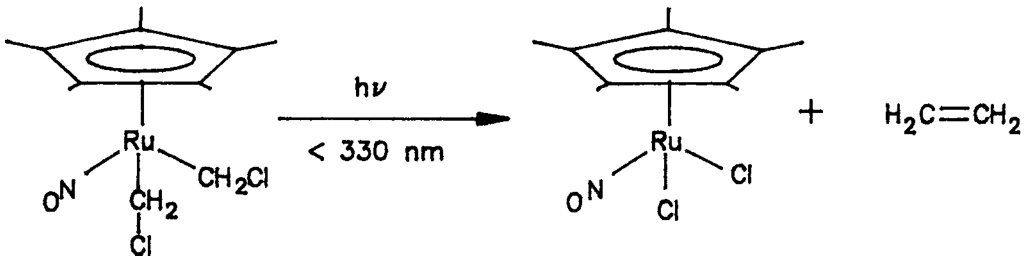
9. Rhodium, A-Frame Dimers. A series of compounds that we have examined are A-frame dirhodium complexes. The complexes contain the pyrazolate anion in the apex position, bis(diphenylphosphino)methane (dppm), (diphenylarsino)(diphenylphosphino)methane (dapm) or bis(diphenylarsino)methane (dpam) as transoid bridging ligands, and t-BuCN as legs of the structure as illustrated below. The Rh_2^+ dimers were found to luminesce weakly in methylene chloride and displayed oxidative electrochemistry.



The Rh_2^{2+} complexes were oxidized by controlled potential electrolysis yielding paramagnetic Rh_2^{3+} dimers which were exmained by ESR spectroscopy. Solutions of the Rh_2^{3+} species in 4:1 CH_2Cl_2/toluene at room temperature were green and exhibited a single isotropic esr signal near g = 2.15. Frozen solutions of the Rh_2^{3+} species at 77 K were red, except for the complex having the

3,4,5-tribromopyrazolate bridge which remained green. The change from the green form with the unpaired electron density localized over two equivalent nuclei to the red form with electron density localized on one of the ligands was suggested by a dominant g-value of 1.99. This color change was attributed to structural rearrangements rather than electronic effects which would require a change in the oxidation state of the metal centers.

10. "Piano-Stool" Complexes. An initial investigation into the photochemical extrusion of ethylene from Cp*Ru(NO)(CH_2Cl_2)$_2$ as illustrated in eq. 6 was carried out. The compound itself

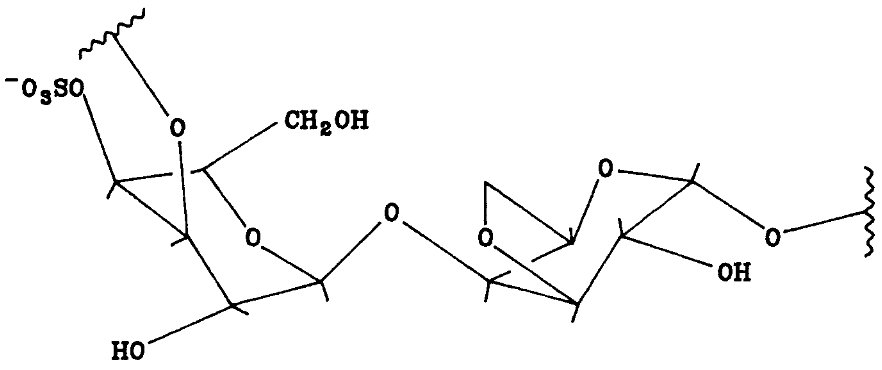


(6)

was found to be thermally unstable in the solid state and decomposed to a material, which, when dissolved in methylene chloride, was converted into the dichloro complex upon addition of HCl. Spectral changes for steady state photolysis at 366 nm of the complex in methylene chloride revealed that the reaction most likely occurs stepwise rather than concerted as originally thought. Smooth absorption changes from the spectrum of Cp*Ru(NO)(CH_2Cl)$_2$ to the one for Cp*Ru(NO)Cl_2 did not occur. Rather the absorbance at 371 nm actually increased rather than decreased as would be expected for the direct conversion of Cp*Ru(NO)(CH_2Cl)$_2$ into Cp*Ru(NO)Cl_2.

Applications

1. Surface Modified Electyrodes-Hydrogels. Platinum and gold working electrodes were modified with the hydrogel kappa-carrageenan shown below. This hydrogel is an anionic



D-galactose-4-sulfate **3,6-anhydro-D-galactose**

polysaccharide extracted from seaweed. The hydrogel was cured on the electrode surface with ruthenium(II) trisbipyridine and methyl viologen. In the presence of triethanolamine (TEOA), the following sequence of reactions were postulated to occur upon illumination of the modified electrode with light. Photolysis at 436 nm gave rise to a significant photocurrent which depended on the

$$[Ru(bpy)_3]^{2+} \xrightarrow{h\nu} [Ru(bpy)_3]^{2+*} \tag{7}$$

$$[Ru(bpy)_3]^{2+*} + MV^{2+} \longrightarrow [Ru(bpy)_3]^{3+} + MV^{+} \tag{8}$$

$$[Ru(bpy)_3]^{3+} + TEOA \longrightarrow [Ru(bpy)_3]^{2+} \text{ Oxidation Prod.} \tag{9}$$

$$MV^{+} \xrightarrow[\text{electrode}]{} MV^{2+} + e^{-} \tag{10}$$

concentrations of $[Ru(bpy)_3]^{2+}$, MV^{2+} and triethanolamine. The maximum photocurrent obtained was 12 $\mu a/cm^2$.

The behavior of the modified electrode was also examined in water with MV^{2+} replaced by O_2. The type of photocurrent (oxidative or reductive) depended on the pH of the solution and the offset potential of the working electrode. The maximum photocurrent of 12 $\mu a/cm^2$ was obtained with a 4% carrageenan hydrogel cured with 5 mM $[Ru(bpy)_3]^{2+}$ in 50 mM KNO_3, $Po_2 = 1$ atm, an electrolyte solution containing 1 M TEOA in 0.1 M KNO_3 and an excitation wavelength of 436 nm. The mechanism that accounts for the observations is outlined as follows.

$$[Ru(bpy)_3]^{2+} \xrightarrow{h\nu} [Ru(bpy)_3]^{2+*} \qquad (11)$$

$$[Ru(bpy)_3]^{2+*} + O_2 \longrightarrow \{Ru(bpy)_3]^{3+} + O_2^- \qquad (12)$$

$$O_2^- + H^+ \xrightarrow{H^+} HO_2 \qquad (13)$$

$$[Ru(bpy)_3]^{2+*} + HO_2 \xrightarrow{H^+} H_2O_2 + [Ru(bpy)_3]^{3+} \qquad (14)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (15)$$

$$H_2O_2 \qquad H^+ + HO_2^- \qquad (16)$$

$$HO_2^- + OH^- \xrightarrow[\text{electrode}]{} O_2 + H_2O + 2e^- \qquad (17)$$

$$[Ru(bpy)_3]^{3+} + TEOA \longrightarrow [Ru(bpy)_3]^{2+} + \text{Oxid. Prod.} \qquad (18)$$

The E° values for the redox couple in eq. 17 is 0.076 V in 1 M OH^- and the pKa of H_2O_2 is 11.6. Superimposed on the photocurrent is a background current due to the process represented in eq. 17 (reduction of O_2) which becomes less important as the offset potential of the working electrode becomes more positive.

The relationship between the observed photocurrent and offset potential is consistent with the proposed mechanism. As the offset potential of the working electrode becomes more positive, the oxidative photocurrent produced by the system increases due to the fact that the background current produced at the electrode becomes less significant. The opposite is true as the offset potential becomes more negative. More O_2^- is produced at the electrode surface as indicated by the increase in background current. The O_2^- oxidatively quenches the excited state of $[Ru(bpy)_3]^{2+*}$ according to eq. 14 resulting in the observed reductive photocurrent.

The fact that the photocurrent increases as the partial pressure of O_2 increases in the system is also consistent with the proposed mechanism. The rate of O_2^- excited state quenching of $[Ru(bpy)_3]^{2+*}$ or its rate of reaction at the electrode surface to give O_2^- would be enhanced by an increase in the concentration of O_2.

Perhaps the most revealing evidence supporting the proposed mechanism is the dependence of the photocurrent on pH. A plot of the photocurrent vs. pH is sigmoidal much like an acid-base titration curve. The change in slope of its derivative occurs at pH = 11.5 which is approximately equal to the pK_a of H_2O_2. Thus, the oxidative photocurrent depends on the concentration of HO_2^- in solution. At low HO_2^- concentrations, reductive photocurrent is observed due to preferential reduction of O_2 at the electrode surface to form O_2^- which then quenches the excited $[Ru(bpy)_3^{2+*}$ according to eq. 14 resulting in the observed reductive photocurrent.

2. <u>Carbon Dioxide Reduction</u>. The discovery that the nonstoichiometric compound of composition $[Co_{1.2}(Mebpy\text{-}Mebpy)_2](PF_6)_{2.4}$ deposited on the electrode surface upon reductive cycling in acetonitrile as shown in Figure 2 prompted an investigation into catalyzed CO_2 reduction in acetonitrile at a bare platinum electrode, at a bare platinum electrode in a solution containing $[Co(bpy)_3]^{2+}$ as a homogeneous catalyst and at a surface modified electrode of composition $[Co_{1.2}(Mebpy\text{-}Mebpy)_2](PF_6)_{2.4}$ as described above. The predominate product obtained in the electrolysis was oxalate ion.

Table III lists the results of those experiments. While the study is only in its initial stages, the most unusual observation is the data related to a freshly polished platinum surface where catalysis clearly is indicated as noted by the data in Table III. The presence of $[Co(bpy)_3]^{3+}$ in solution speeds up electrochemical processes, but not the production of oxalate ion. This data is ambiguous, however, since the experiments were effected prior to our discovery about the precarious nature of the electrode surface. This line of research is encouraging given that the modified electrode did indicate catalysis. Whether this is related to the presence of the cobalt complex or is only due to the platinum surface remains to be determined.

Table III. Oxalate Production Under Varying Conditions

	Bare Pt Electrode[a]	
Current (Coul)	Analyzed, ppm	Theo (from current), ppm
0.02714	2.1	1.24
0.04731	2.0	2.16
0.05960	1.4	2.72
0.03668[b]	10.1	1.67
0.03166[b]	15.2	1.44
	Bare Pt Electrode-[Co(bpy)$_3$]$^{2+}$ Solution	
0.3914	1.4	17.8
1.277[c]	23	58.3
	Surface Modified Electrode	
0.27[d]	20.4	12.3

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a. Electrolysis effected at E = -1.700 V vs SSCE, time = 15 min, unless otherwise noted, electrode was a Pt billet (diameter of 6 mm, area of 28 mm^2).

b. Freshly polished surface (0.25 μ polishing compound).

c. time - 17 min., 50 μL - methods added.

d. time - not documented.

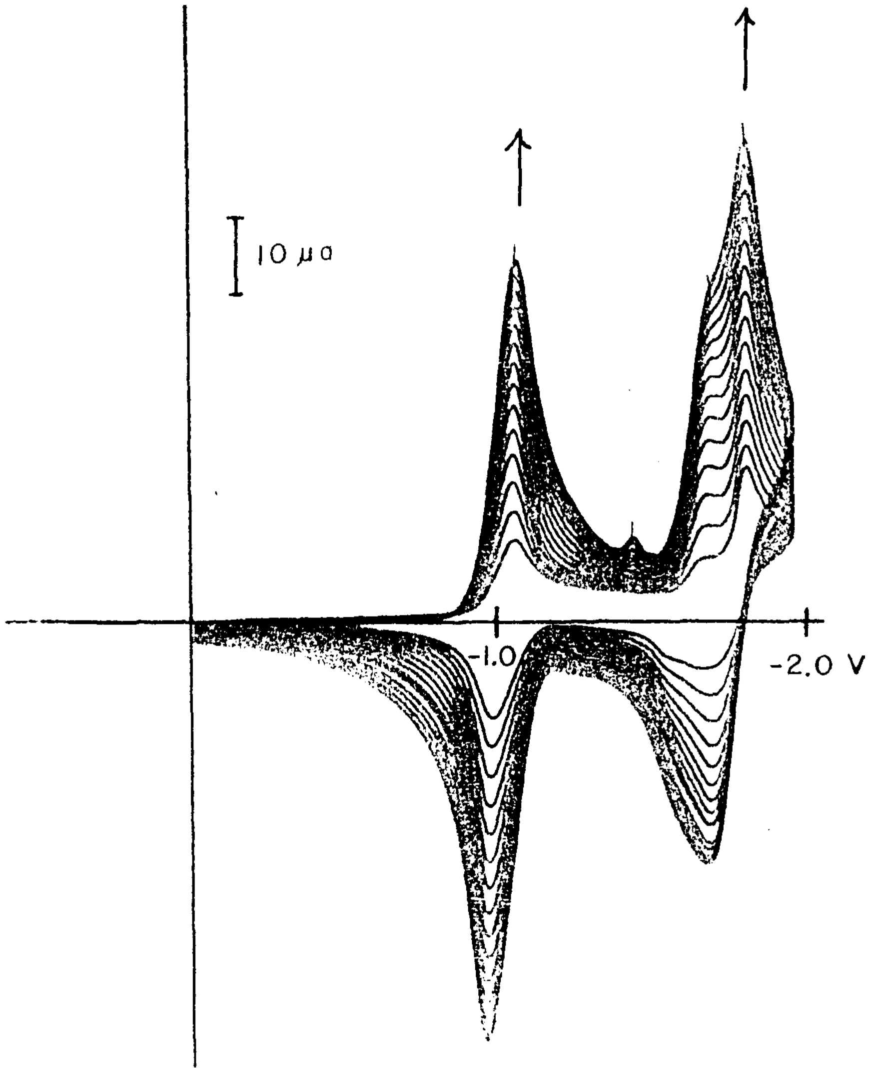

Figure 2. Growth of material deposited on a Pt electrode from an acetonitrile solution containing $[Co_{1.2}(Mebpy-Mebpy)_2](PF_6)_{2.4}$. The potential is in V. vs. SSCE; the sweep rate is 200 mV/s; the electrolyte is 0.1M TBAH.